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THE DYNAMIC BEHAVIOUR OF A FIXED BED ADSORBER

Thesis

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by

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Abstract

A mathematical model describing the dynamic behaviour of a fixed-bed adsorber has been constructed, based upon the physical characteristics of the air-CO_2-molecular sieve system. A non-linear adsorption isotherm, diffusion into the pellets and sorbed phase diffusion have been incorporated in the model. The resulting partial differential equations have been integrated with the aid of a computer programme using finite difference methods.

A series of experimental adsorption runs (using the air-CO_2-molecular sieve system) has been performed in which the dimensionless groups which describe the behaviour of the system were systematically varied. Gas concentration histories for a number of bed lengths were obtained from each run.

Agreement between the computed and experimental results was obtained.

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Errata

p. 2	7th line from bottom: after "sieve" insert "5A"
p. 18	8th line from bottom: for "pore" read "pellet"
p. 30	2nd line: for "1/2000" read "1/350"
p. 108	7th line from bottom: for "approximately" read "appropriately"
p. 111	2nd line: after "concentration" insert "constant".

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Chapter 1

ADSORPTION AS A UNIT OPERATION OF CHEMICAL ENGINEERING

Adsorption has been defined [1] as that operation which deals primarily with the utilization of surface forces for the concentration of materials on the surfaces of solid bodies, referred to as adsorbents. Adsorption may be distinguished from absorption in that the former does not entail chemical reaction between sorbent and sorbate, while the latter refers to a more or less permanent chemical reaction. Because adsorption takes place on the surface of a solid, practical adsorbents must have large surface area to volume ratios, and the cavities implied by this condition must be reasonably accessible. A wide range of solids which fulfil these conditions has been developed for industrial use in the fractionation of mixtures of fluids. They are usually granular in form and are supported in beds of suitable geometry through which the mixture to be fractionated is passed.

In general, some of the components of the mixture are almost completely adsorbed, while the rest of the components are not adsorbed and so pass out of the bed

to form the effluent. However this degree of separation cannot continue indefinitely - eventually the adsorptive capacity of the bed will begin to be depleted and the components which had previously been adsorbed will begin to appear in the effluent. It is usually desirable to stop the flow before this "breakthrough" occurs. Semi-continuous operation can usually be achieved by switching the flow to an identical bed while the first one is "regenerated". The desorption involved in this process is commonly achieved by raising the temperature of the adsorbent or by lowering the partial pressure of the adsorbate.

Factors governing the design of adsorption equipment are:

1. the adsorption equilibrium for adsorbate on adsorbent
2. the processes determining the rate of adsorption
3. the physical state and geometrical configuration of adsorbent

1. For the two-component system of adsorbate and adsorbent, adsorption equilibrium data may be represented by a surface in the three-space of quantity adsorbed (usually in weight per cent of solid), pressure, and temperature. When the adsorbate is present as a small percentage of a gaseous mixture, the ideal mixture law is approximately

valid, and so partial pressure of the adsorbate may be used in place of the pressure coordinate without altering the equilibrium surface. For the fixed-bed adsorption process, small adsorbate concentrations also mean that the heat-of-adsorption phenomenon will cause only a very slight rise in adsorbent temperature. It is therefore possible, in any particular case, to represent sufficient equilibrium data by a single "adsorption isotherm" for the temperature concerned. This assumption of isothermality is a most important simplification, since without it a mathematical model of the process becomes an order of magnitude more complex. Fortunately, though, for most of the separations for which adsorption is used, this simplification is based on valid assumptions.

2. The various processes which determine the dynamics of the adsorption operation may be illustrated by following the progress of a single molecule of adsorbate from the time it enters the bed until it finally comes to rest in the sorbed phase.

The molecule will first travel through the bed for some distance in the bulk flow of the fluid between the pellets. Eventually it will stop at one particular pellet and begin to diffuse through the stagnant layer of gas which surrounds it. When it reaches the surface of the

pellet it is not likely to be adsorbed at once, but will probably enter one of the "pores" in the pellet and diffuse towards its centre. At some point along the pore, adsorption will take place. Again, it is unlikely that the molecule will stop here: diffusion in the sorbed phase may well occur.

From this it may be seen that there are four rate determining processes involved: diffusion through the film surrounding the pellet, diffusion along the pores of a pellet, adsorption, and diffusion in the sorbed phase. Fortunately not all of these are always significant. The actual adsorption process may usually be thought of as instantaneous without introducing significant error. Of the other three processes usually one, often two, may be neglected as rate determining processes.

3. As previously mentioned, the adsorbent is usually in granular form. Reducing the size of the granules reduces the resistance due to diffusion into them but increases the pressure drop of the bulk flow of fluid through the bed. These considerations usually result in pellets with dimensions of the order 0.5 cm.

The vessel used to contain the adsorbent, "the adsorber", usually takes the form of a vertical cylinder with fluid flow parallel to the axis. To avoid the danger

of particle attrition, the sense of the process flow is usually dictated by the principle that the flow most liable to cause attrition should be downward, i.e. if the reactivation flow rate must exceed the process flow in this respect, then the process flow will be from bottom to top and the reactivation flow from top to bottom.

The pressure and temperature selected for the operation of the adsorber are often determined solely by those of the mixture to be fractionated. Occasionally it is necessary to alter the operating conditions, by increasing the pressure or by lowering the temperature, in order to reduce the weight of adsorbent required to an acceptable level. The dynamics of the process will also be affected by changes of pressure and temperature but it is unlikely that this will influence the choice of operating conditions.

Because of the dynamic character of the adsorption process, the mathematics which describe it are necessarily complex. At present, many adsorbers are designed by quite crude methods, relying heavily on previous industrial experience, and relatively generous safety factors. However, three factors are combining to render this technique inadequate: larger plant sizes and more expensive

adsorbent materials are combining to increase the cost of overdesign, and the availability of high speed computers is making the solution of the complex mathematical models of the process a more practical proposition.

It has therefore become necessary to formulate mathematical models and to test their usefulness in the prediction of adsorber behaviour. Chandrasekharan [2A] has made an excellent survey of some proposed models, and he also tested the validity of some of them for the air-CO_2-molecular sieve 4A system. He concluded that Rosen's [3,4] model was the best available, but that, because it used a linear isotherm, it was not really satisfactory in cases where the isotherm could not be linearized.

The present work may therefore be seen as an attempt to devise a model and an associated system of computation which will admit a non-linear isotherm, and thus yield a better description of the behaviour of the air-CO_2-molecular sieve system.

Chapter 2

EXAMINATION OF THE PHYSICAL SYSTEM AND THE FORMULATION OF A MODEL

As a frame-work for the formulation of the model, it is useful to return to the description of the progress of a single molecule of adsorbate from the time it enters the bed until it comes to rest in the sorbed phase.

The velocity of the bulk flow of gas down the length of the vessel will be determined by the volumetric flow rate of the gas, the crossectional area of the bed, and the void fraction of the bed. It will be modified by the gas which is removed by adsorption, i.e. the ratio of the influent flow rate to that of the effluent will be the inverse ratio of the mole fractions of the non-sorbed gas in the influent and effluent. However, when the concentration of sorbate in the mixture is small this effect is entirely negligible. The molecule may thus be assumed to move with the bulk flow velocity, except in so far as it is subject to longitudinal diffusion. However, computations based on the experimental results of Chandrasekharan and of the author confirm that this effect, too, is negligible for the system studied. The

resistance to mass transfer due to diffusion in the boundary layer surrounding each pellet will vary with the Schmidt and Reynolds numbers of the system. Because of the previously mentioned restrictions on pellet size and gas flow rate, it is unlikely that the relative importance of this mechanism will vary appreciably from one adsorption process to another. By comparison of his experimental results with Rosen's curves for various values of this resistance, Chandrasekharan [2B] showed that the best fit could be obtained by choosing a film resistance of zero, thus suggesting that film diffusion was not a rate determining process for the air-CO_2-molecular sieve system that he studied. Using this as a basis, it has been shown in Appendix A that it is reasonable to neglect film resistance in the formulation of the present model. Thus far the model is very simple - any complications which arose having been discarded as "negligible". However, once inside the pellet things become more complex, so it is probably best to try to describe the physical system in some detail.

The pellets studied were of two sizes: one batch of 1/8" diameter and 0.15" long, and the other batch 1/16" diameter and 0.135" long. Each pellet is made up of several billion molecular sieve crystals. Each crystal is the

shape of a cube with the corners missing [5A]. They have a size distribution of 0.1 to 2μ [5B]. The crystals are held together to form the pellet by means of a clay binder. Little information is presently available about the nature of this binder [5C]. However, from the fact that too generous use of binder will result in

(a) reduced adsorbent capacity due to encased crystals

(b) reduced diffusion rates due to blocked pores and partially encased crystals

(c) increased adsorbent weight

one may conclude that it is used sparingly and may therefore be ignored for the purposes of model formulation. This is not to say, though, that its presence cannot be allowed for by the adjustment of parameters at a later stage.

One is now left with a pellet made up of crystals and interstices. If the diffusion coefficients of the crystals and the interstices are comparable, a most complex regime will exist for diffusion in a pellet, involving three distinct modes of flow, as described by J.M. Smith et al [7,8,9]. However, because of the extremely small diffusion coefficient of molecular sieve crystals, (Dworjanyn suggests 3.5×10^{-10} cm^2/sec) [5D] it is entirely

satisfactory to postulate a series diffusion process in which diffusion takes place first along the interstices, or "pores", in the gas phase, and only later inside the crystals in the sorbed phase.

The dimensions of the crystals, and by inference, of the interstices, suggest that the pore diffusion will be of a gaseous nature (rather than Knudsen). The pore diffusion coefficient derived by Dworjanyn [5E] from his experimental work seems to bear this out, as it is roughly comparable to that for free gaseous diffusion. The isotropic character of the pellet suggests that an overall value of an "effective pellet diffusion coefficient", with no conscious reference to pore radius or tortuosity factor will be adequate to describe the process.

Adsorption is usually understood to have occurred when the molecule in question ceases to move with thermal motion in the gas phase, and becomes attached more or less permanently to the surface of the adsorbent. In the case of molecular sieves the phenomenon involved is quite different and probably bears discussion. The schematic plot of molecular potential vs distance for a CO_2 molecule at the edge of a crystal of molecular sieve shown in Fig. 1 may help to illustrate the situation.

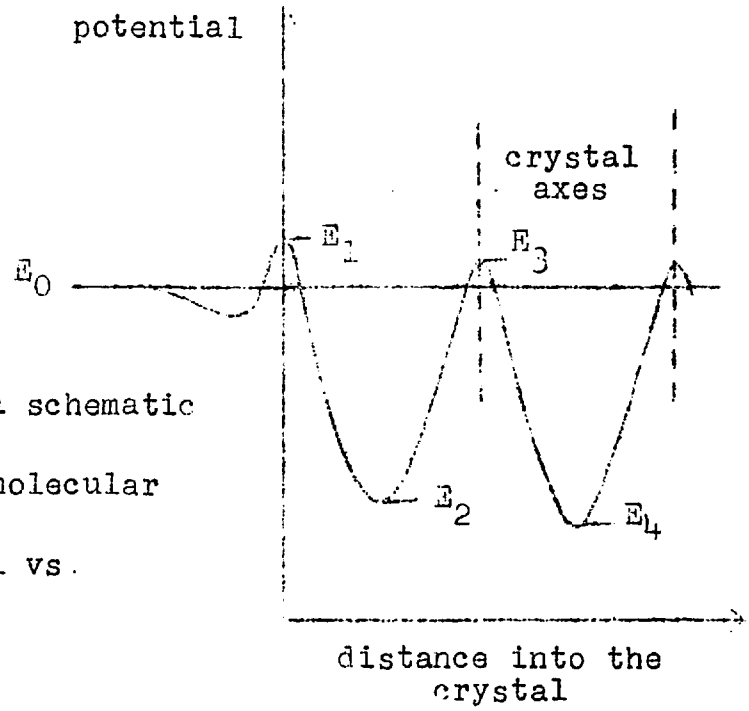


Fig. 1 A schematic plot of molecular potential vs. distance

Although Whitford's [6] work on the calculation of these potentials has been confined to cages far from the surface of the crystal, his results may be usefully applied in this discussion to yield qualitative conclusions. Referring to Fig. 1 again, he has shown that E_3 is only very slightly greater than E_0, but that E_4 is very much less that E_0. If one now assumes that E_2 will be not very different from E_4, and similarly for E_1 and E_3, one may draw the following conclusions:

1. The resistance to adsorption, which is related to $E_1 - E_0$, will be very small.

2. The resistance to diffusion in the crystal, which is related to $E_3 - E_4$ is very large.

It therefore seems reasonable to neglect any resistance due to the adsorption process, and to consider only the much slower diffusion process inside the crystal.

The shape and sizes of the crystals have been described earlier. As it would be very difficult to deal with cubes mathematically (for reasons that will be mentioned later), and since it would be even harder to determine and utilize the size distribution function of the crystals [5B], it was decided to treat the crystals as though they were spheres of a uniform radius. This is certainly the crudest assumption made so far, and one hopes that it will not affect the usefulness of the model too adversely.

Dworjanyn [5F] speculated on the effects of the small cages on the equation for diffusion between the large ones. He derived an equation of similar form to Fick's Law, but with an additional "sink" term to represent the effect of the small cages. He did not test this model experimentally, and Whitford's [6] work has since shown that the potential in the small cages is too high for a CO_2 molecule to get in anyway. So Dworjanyn's equation

reduces again to Fick's Law.

The various assumptions and simplifications made thus far may now be collected and presented in the form of a description of "the model":

The adsorber is a cylinder filled with pellets. There are no radial effects in the adsorber so that the only relevant dimension is the length L. The void fraction is V_o and the velocity of the gas, based on the ratio of the volumetric flow rate to the crossectional area of the adsorber, is V. The residence time E of the gas in the adsorber is therefore $\frac{LV_o}{V}$.

The pellets are infinite cylinders, or spheres, or a compromise between the two forms, of radius S. (This statement will be explained later.) Gaseous diffusion occurs in the pores of the pellets, according to Fick's Law: $\frac{\partial C}{\partial t} = D_p \nabla^2 C$, where C is the concentration of CO_2 in the gas phase, and D_p is the pore diffusion coefficient. Pellets are small enough to assume that there is a uniform concentration over the surface of any one pellet. Each pellet is made up of vast quantities of crystals, in such a way that all surfaces of the crystals face onto pores.

The crystals are spheres of uniform radius s. Diffusion in the sorbed phase occurs in the crystals according to Fick's Law: $\frac{\partial w}{\partial t} = D_c \nabla^2 w$, where w is the concentration

of CO_2 in the sorbed phase and D_c is the crystal diffusion coefficient. The crystals are also small enough to assume that variation of concentration occurs only in the radial direction.

The two types of diffusion just described are the only impediments to mass transfer. The concentration of CO_2 in the bulk flow of gas through the adsorber is therefore identical with that in the gas phase at the surface of the pellets. Similarly, the concentration in the gas phase in the pores is in equilibrium with that of the sorbed phase at the surface of the crystals.

The schematic diagram in Fig. 2 may help to illustrate these assumptions. Variations of concentration with distance have been shown in this diagram as continuous functions. However, it is known that the physical system is particulate on a number of levels:

the bed is made up of pellets

the pellets are made up of crystals

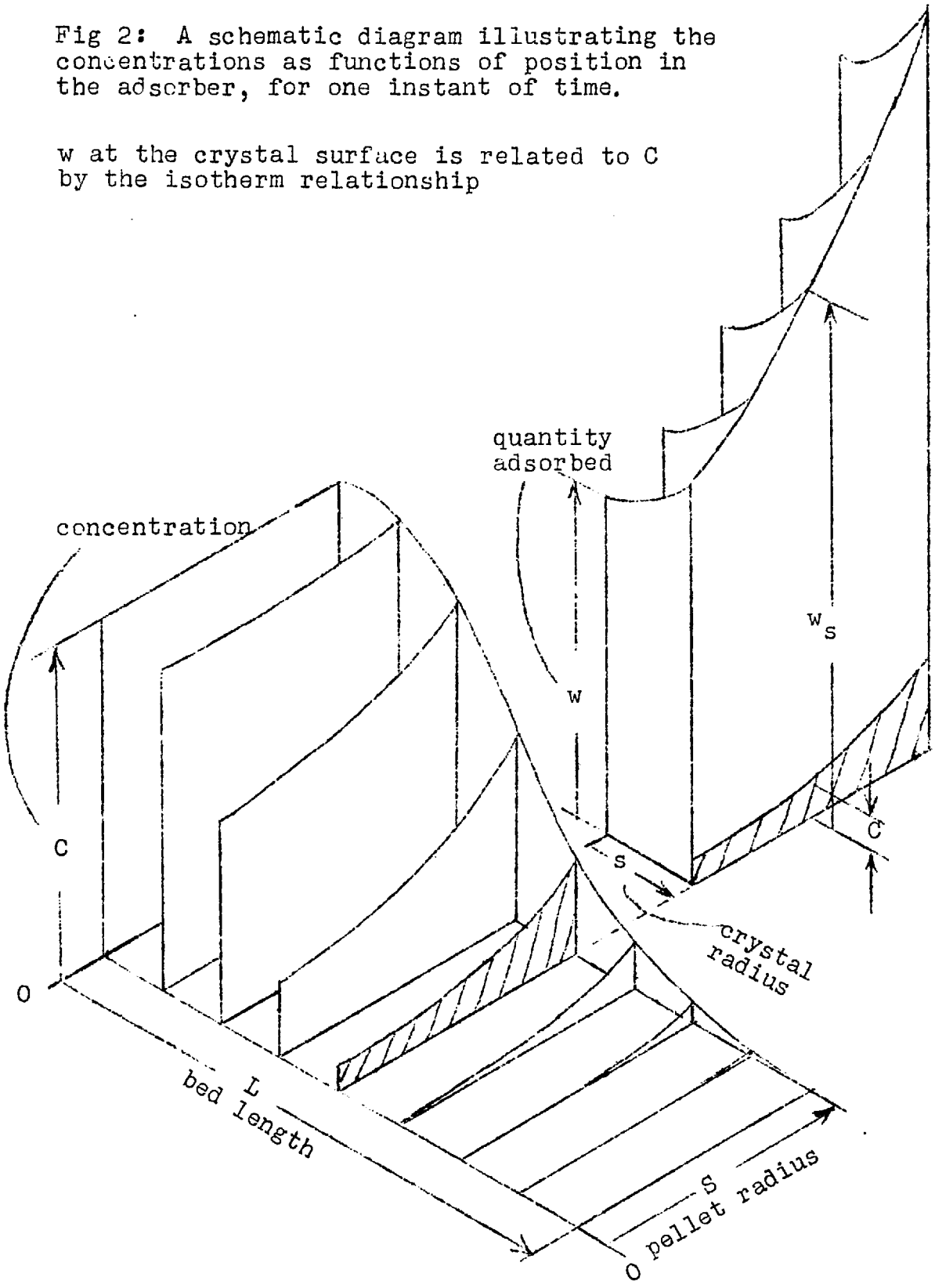
the crystals are made up of cages

the cages are made up of atoms.

But due to the small size of the particles relative to the body of which they are a part, one may, for the purpose of the derivation of differential equations, assume that the particle size is infinitely small. Later, when

Fig 2: A schematic diagram illustrating the concentrations as functions of position in the adsorber, for one instant of time.

w at the crystal surface is related to C by the isotherm relationship



finite difference methods are used to solve these equations, these smooth curves are broken up into a number of discrete points, and it is tempting, and probably not misleading, to think of each point as representing a single particle.

Chapter 3

DERIVATION OF EQUATIONS TO DESCRIBE THE MODEL

Examination of the proposed model reveals that four equations will be needed to describe it mathematically:

1. A mass balance equation for the flow of gas through the bed. This will equate the rate of change of composition of the gas mixture with length and time with the rate of flow of adsorbate into the pellets.
2. An equation for the diffusion of adsorbate in the pores of the pellet, containing a sink term to represent adsorption into the crystals.
3. An isotherm relation between the concentration of the gas in the pores and the amount in the sorbed phase at the surface of the crystals.
4. Finally, another diffusion equation for the sorbed phase in the crystals.

For convenience, the equations will be considered in the reverse order:

The Crystal Equation

Fick's Law may be written: $\frac{\partial X}{\partial t} = D\nabla^2 X$, where X is the concentration of the diffusing substance, D is the diffusion coefficient of the binary pair in which the

diffusion is occurring, and t is time. For a sphere: $\nabla^2 X = \frac{\partial^2 X}{\partial r^2} + \frac{2}{r}\frac{\partial X}{\partial r}$. The crystal diffusion equation may therefore be immediately written:

$$\frac{\partial w}{\partial t} = D_c \left[\frac{\partial^2 w}{\partial r^2} + \frac{2}{r}\frac{\partial w}{\partial r}\right] \qquad \ldots (1)$$

Here, D_c is the crystal diffusion coefficient, r is the dimension for crystal radius and w is the concentration of CO_2 in the sorbed phase.

The Isotherm

Adsorption isotherms are usually available as plots of q versus p (where $q = \frac{\text{weight of adsorbed substance}}{\text{weight of adsorbent}} \times 100\%$ and p is the partial pressure of the substance to be adsorbed - in millimeters of mercury for example.) Although it will later be seen that it is not strictly necessary to resort to an approximating equation to represent these plots mathematically, this is the method which has been used in this work. There were two not entirely complementary reasons for this choice: the Linde data for the adsorption of CO_2 on molecular sieve 5A could be reasonably well fitted by an equation of the form: $q = A + B \ln(p)$, and, for reasons discussed at length later, this data is somewhat suspect, so it was not deemed worthwhile to use any more accurate means of representation.

In whatever form the isotherm is expressed, it will be more convenient if it is dimensionless. This may be done in the following manner:

(Assuming isotherm data to be available in the form of plots of q against p)

Let $\gamma = \frac{\text{moles of } CO_2}{\text{c.c of gas}} = \frac{p}{22.4 \times 1000 \times 760}$

and let $\varphi = \frac{\text{moles of } CO_2}{\text{c.c of solid}} = \frac{q\rho_c}{100 \times 44}$

where ρ_c = crystal density in grams/c.c.

Now let $C = \frac{\gamma}{\gamma_o}$ - where γ_o = feed concentration

and let $w = \frac{\varphi}{\gamma_o}$ Both C and w will be dimensionless

$$C = \frac{p}{p_o}, \quad w = \frac{q\rho_c \times 22.4 \times 1000 \times 760}{p_o \times 44 \times 100} = 3869 \frac{q\rho_c}{p_o}$$

$$\text{or } p = Cp_o, \quad q = w \frac{p_o}{3869\rho_c}$$

These can now be substituted into the isotherm equation to render it dimensionless.

For example, the Linde isotherm for CO_2 on molecular sieve type 5A at 0^oC can be reasonably well fitted by the following equation:

$q = A + B \ln p$ where A = 8.38

B = 1.875

substituting for q and p,

$$w = \frac{3869 f_c}{p_o} (A + B \ln p_o) + \frac{3869 f_c B}{p_o} \ln C$$

i.e. if $A' = \frac{3869 f_c}{p_o} (A + B \ln p_o)$, $B' = \frac{3869 f_c B}{p_o}$

$$w = A' + B' \ln C$$

In order that w should be zero when C is zero, this equation may be altered to

$$w = A' + B' \ln (\epsilon + e^{-A'/B'})$$

without significantly affecting the accuracy of the fit.

The Pellet Equation

To return again to Fick's Law; for a cylinder it may be written:

$$\frac{\partial X}{\partial t} = D \left[\frac{\partial^2 X}{\partial r^2} + \frac{1}{r} \frac{\partial X}{\partial r} + \frac{\partial^2 X}{\partial z^2} \right]$$

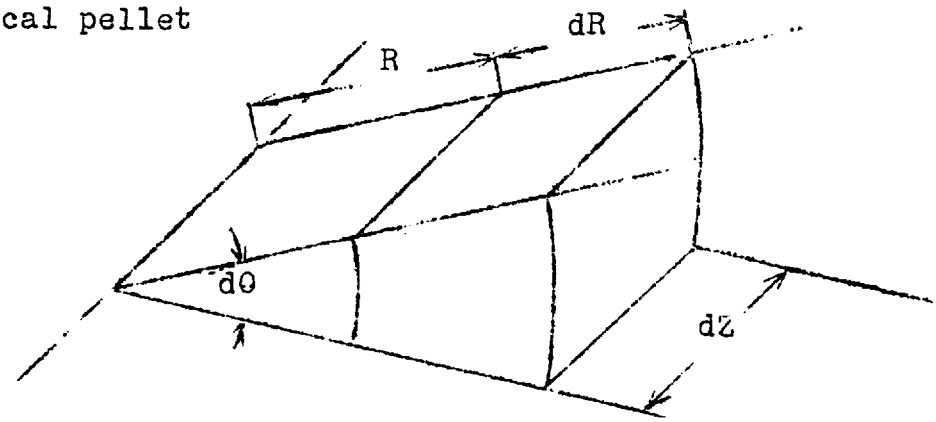
This equation considers X = X(r,z,t), but for an infinite cylinder the last term vanishes and one has the much simpler form: X = X(r,t). Because it was found to be necessary to solve this equation by finite difference methods (rather than by analytic means), it was thought that the extra term which allowed variation of X with z was more of a luxury than could be justified in terms of computing time and space. It was therefore decided to

use an equation of the form:

$$\frac{\partial X}{\partial t} = D\left[\frac{\partial^2 X}{\partial r^2} + \frac{\alpha}{r}\frac{\partial X}{\partial r}\right]$$

where α is an empirical constant lying between 1 and 2. (Hence the previous description of a pellet as a compromise between a sphere and an infinite cylinder.) The computation of the values of α actually used will be found in Appendix B.

Consider now a wedge taken from an infinite, cylindrical pellet



An infinitesimal element from this wedge will have the volume:

$$dV = \left[(R + dR)^2 - R^2\right]\frac{d\theta}{2}\,dz$$

If this element contains dN crystals, each with a radius of s, the total volume of these crystals $dV_c = dN\,\frac{4\pi s^3}{3}$. The volume of the pores dV_p will be $dV - dV_c$. The areas of the two curved faces of the element are: $(R + dR)d\theta dz$

and $RdΘdZ$. The total area of the crystals is $dN\ 4\pi s^2$.

One may now write down a mass balance equation for the sorbate from the following facts:

The flow into the element will be $D_p(R + dR)dΘdZ\left(\frac{\partial C}{\partial R}\right)_{R + dR}$

The flow out will be $D_p RdΘdZ\left(\frac{\partial C}{\partial R}\right)_R$

The quantity accumulated in the pores will be $dV_p\left(\frac{\partial C}{\partial t}\right)$

The quantity adsorbed by the crystals will be $D_c dN\ 4\pi s^2\left(\frac{\partial w}{\partial r}\right)_s$

The equation is therefore:

$$D_p dΘdZ\left[R\left(\frac{\partial C}{\partial R}\right)_{R + dR} - R\left(\frac{\partial C}{\partial R}\right)_R + dR\left(\frac{\partial C}{\partial R}\right)_{R + dR}\right] =$$

$$dV_p\left(\frac{\partial C}{\partial t}\right) + D_c\ dN\ 4\pi s^2\left(\frac{\partial w}{\partial r}\right)_s$$

Now $\left(\frac{\partial C}{\partial R}\right)_{R + dR} - \left(\frac{\partial C}{\partial R}\right)_R = dR\left(\frac{\partial^2 C}{\partial R^2}\right)$

and in the expression for $dV = RdRdΘdZ + \frac{dR^2 dΘdZ}{2}$,

the second term may be dropped to give:

$$dΘdZ = \frac{dV}{RdR}$$

The left hand side may now be simplified to yield:

$$D_p \frac{dV}{RdR}\left[RdR\left(\frac{\partial^2 C}{\partial R^2}\right) + dR\left(\frac{\partial C}{\partial R}\right)\right]$$

or $$dVD_p\left[\frac{\partial^2 C}{\partial R^2} + \frac{1}{R}\left(\frac{\partial C}{\partial R}\right)\right]$$

The right hand side may also be simplified

$$(dV - dV_c)\frac{\partial C}{\partial t} + D_c\left(\frac{3}{s}\right) dV_c \left(\frac{\partial w}{\partial r}\right)_s$$

so that the equation becomes

$$D_p\left[\frac{\partial^2 C}{\partial R^2} + \frac{1}{R}\frac{\partial C}{\partial R}\right] = \left(1 - \frac{dV_c}{dV}\right)\frac{\partial C}{\partial t} + \frac{3D_c}{s}\left(\frac{dV_c}{dV}\right)\left(\frac{\partial w}{\partial r}\right)_s$$

The $\frac{1}{R}$ in the first term may now be replaced by $\frac{\alpha}{R}$.

If the two terms on the right hand side are compared, the $\frac{\partial C}{\partial t}$ term will be seen to be negligible.

The ratio of these terms may be written: $\left(\frac{dV}{dV_c} - 1\right)\frac{s}{3D_c}\frac{\frac{\partial C}{\partial t}}{\left(\frac{\partial w}{\partial r}\right)_s}$

From the previously mentioned isotherm equation,

$\frac{\partial C}{\partial t} = \frac{C}{B}\left(\frac{\partial w}{\partial t}\right)_s$. So the ratio becomes: $\left(\frac{dV}{dV_c} - 1\right)\frac{sC}{3D_cB}\frac{\left(\frac{\partial w}{\partial t}\right)_s}{\left(\frac{\partial w}{\partial r}\right)_s}$

If the crystal equation is rewritten as follows:

$$\frac{\frac{\partial w}{\partial t}}{\left(\frac{\partial w}{\partial r}\right)_s} = \frac{D_c}{s}\left[\frac{s\left(\frac{\partial^2 w}{\partial r^2}\right)_s}{\left(\frac{\partial w}{\partial r}\right)_s} + 2\right]$$

it may be substituted into the expression for the ratio of the two terms.

The ratio then becomes:

$$\left(\frac{dV}{dV_c} - 1\right)\frac{C}{3B}\left[\frac{s\left(\frac{\partial^2 w}{\partial r^2}\right)_s}{\left(\frac{\partial w}{\partial r}\right)_s} + 2\right]$$

An upper limit for the expression in the brackets may be obtained with the help of finite difference approximations for the two derivatives:

$$\left(\frac{\partial^2 w}{\partial r^2}\right)_s = \frac{w_{s+1} - 2w_s + w_{s-1}}{(\Delta r)^2}$$

$$\left(\frac{\partial w}{\partial r}\right)_s = \frac{w_{s+1} - w_{s-1}}{2\Delta r}$$

(where w_{s+1} is a fictitious point outside the surface of the crystal, and s is now the number of steps in crystal radius.)

$$\left[\frac{s\left(\frac{\partial^2 w}{\partial r^2}\right)_s}{\left(\frac{\partial w}{\partial r}\right)_s} + 2\right] = 2s\left(\frac{w_{s+1} - 2w_s + w_{s-1}}{w_{s+1} - w_{s-1}}\right) + 2$$

If a sufficiently large number of steps is taken in crystal radius, $s\left(\frac{w_{s+1} - 2w_s + w_{s-1}}{w_{s+1} - w_{s-1}}\right)$ will not vary significantly with s.

(It has been found in practice that s need never exceed 5.)

Now since w is a monotonically increasing function of r, $\left(\frac{w_{s+1} - 2w_s + w_{s-1}}{w_{s+1} - w_{s-1}}\right)$ can never exceed 1.

It is therefore safe to say that $\left[\frac{s\left(\frac{\partial^2 w}{\partial r^2}\right)_s}{\left(\frac{\partial w}{\partial r}\right)_s} + 2\right]$ will never exceed 12.

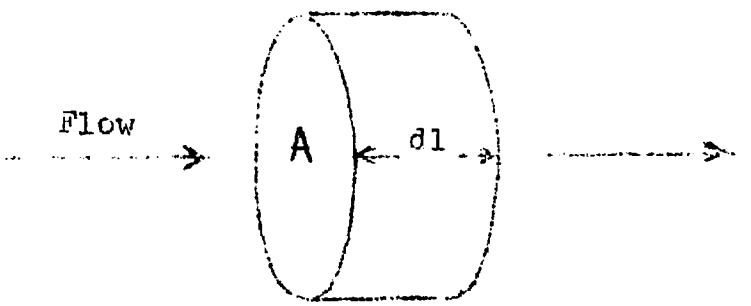
From Dworjanyn[5H] $\left(\frac{dV}{dV_c} - 1\right) \simeq 1$. For adsorption at 20 atm. and $0^\circ C$, with a feed concentration of 500 ppm of CO_2,

$B \approx 1500$. The maximum value of C is 1. The maximum value of the ratio is therefore about 1/2000. Thus the second term is entirely negligible - so the final form of the pellet equation becomes:

$$D_p \left[\frac{\partial^2 C}{\partial R^2} + \frac{\alpha}{R} \frac{\partial C}{\partial R} \right] = \frac{3D_c}{s} \left(\frac{dV_c}{dV} \right) \left(\frac{\partial w}{\partial r} \right)_s \qquad \ldots (2)$$

The Bed Equation

In order to derive the mass balance equation for bulk flow in the adsorber, consider the differential element of an adsorber sketched below



In the same manner as before, one may write down the equation:

$$A\, dl\, V_o \left(\frac{\partial C}{\partial t} \right) = V\, A\, (C)_l - V\, A\, (C)_{l+dl} - dA_p D_p \left(\frac{\partial C}{\partial R} \right)_s$$

where A is the crossectional area of the adsorber

V_o is the void fraction of the bed

V is the nominal velocity of the gas and

dA_p is total surface area of all the pellets in this element of the adsorber

Using the expression for the surface area/volume ratio for cylindrical pellets derived in Appendix B, one may evaluate dA_p as follows:

$$dA_p = \left(\frac{\alpha + 1}{S}\right)(1 - V_o)\, A\, dl$$

The second and third terms of the mass balance equation may be combined to form: $-V\, A\, dl\left(\frac{\partial C}{\partial l}\right)$. The element volume $A\, dl$ is now common to all terms, so the equation may be written:

$$V_o\left(\frac{\partial C}{\partial t}\right) + V\left(\frac{\partial C}{\partial l}\right) + \left(\frac{\alpha + 1}{S}\right)(1 - V_o)\, D_p\left(\frac{\partial C}{\partial R}\right)_S = 0$$

Using the same sort of argument as was used in the derivation of the pellet equation, $V_o\left(\frac{\partial C}{\partial t}\right)$ may be compared with the last term on the left hand side - and found to be equally negligible. The last of the basic equations may therefore be written:

$$\left(\frac{\partial C}{\partial R}\right)_S = \frac{-SV}{(\alpha + 1)(1 - V_o)\, D_p}\left(\frac{\partial C}{\partial l}\right) \qquad \ldots (3)$$

The equation for the isotherm has already been made dimensionless. It will be convenient if the other three equations are similarly transformed. This may be accomplished by making the following substitutions:

$r' = r/s$ $\qquad E = \frac{LV_o}{V}$ $\qquad X_R = \frac{s^2}{D_p E}$

$R' = R/S$

$l' = l/L$ $\qquad V_l = \frac{dV}{dV_c}$ $\qquad Y_R = \frac{s^2}{D_c T}$

$t' = t/T$ (where T is an interval of time to be defined later)

The equations then become:

$$Y_R\left(\frac{\partial w}{\partial t'}\right) = \left[\frac{\partial^2 w}{\partial r'^2} + \frac{2}{r'}\frac{\partial w}{\partial r'}\right]$$

$$\frac{3}{V_l}\frac{X_R}{Y_R}\cdot\frac{E}{T}\left(\frac{\partial w}{\partial r'}\right)_l = \left(\frac{\partial^2 C}{\partial R'^2} + \frac{\alpha}{R'}\frac{\partial C}{\partial R'}\right)$$

$$\frac{(\alpha+1)(1-V_o)}{V_o X_R}\left(\frac{\partial C}{\partial R'}\right)_l = -\left(\frac{\partial C}{\partial l'}\right)_l$$

If $w = w(r', R', l', t')$

and $C = C(R', l', t')$

then the initial and boundary conditions are:

$$w(r', R', l', 0) = 0 \quad , \quad w(1, 1, 0, t') = w_o$$

$$C(R', l', 0) = 0 \quad , \quad C(1, 0, t') = 1$$

The system will be completely defined when an isotherm condition is given, such as $w_l = A' + B' \ln (C + e^{-A'/B'})$

This completes the formulation of the mathematical model. A means of solving this set of equations will be described in the next chapter.

Chapter 4

DEVELOPMENT OF A COMPUTER PROGRAMME TO SOLVE THE EQUATIONS

There are two ways of solving a differential equation: analytically and with the use of finite difference methods. The first method yields an exact, elegant result, but in only a limited number of cases. The second method does not give an exact result, and in general involves a larger amount of calculation, but its chief virtue is that it is applicable in many cases where the analytic approach fails. Broadly speaking, non-linear equations are not solvable by analytic methods and for this reason the present problem was solved by a finite difference approach. The method is outlined below.

1. Assuming that conditions were known at time t_i, values of $C(R', 1')$ were guessed for time t_{i+1}
2. These values of C were used to evaluate $\left(\frac{\partial C}{\partial 1'}\right)$ and hence, from equation (3), $\left(\frac{\partial C}{\partial R'}\right)_1$
3. The values of C, together with those of $\left(\frac{\partial C}{\partial R'}\right)_1$ were used to evaluate $\left[\frac{\partial^2 C}{\partial_{R'}{}^2} + \frac{\alpha}{R'}\frac{\partial C}{\partial R'}\right]$, and hence, from equation (2) $\left(\frac{\partial w}{\partial r'}\right)_1$

4. These values of $\left(\frac{\partial w}{\partial r'}\right)_1$, together with the known values of w at time t_i, were used to compute the new values of w, at time t_{i+1}, from equation (1).

5. These values of w(r', R', 1') lead to values of C(R', 1'), via the isotherm.

6. This new set of values of C may now be compared with the previously guessed values of C. If there is a significant deviation between these sets of values, the entire cycle may be repeated.

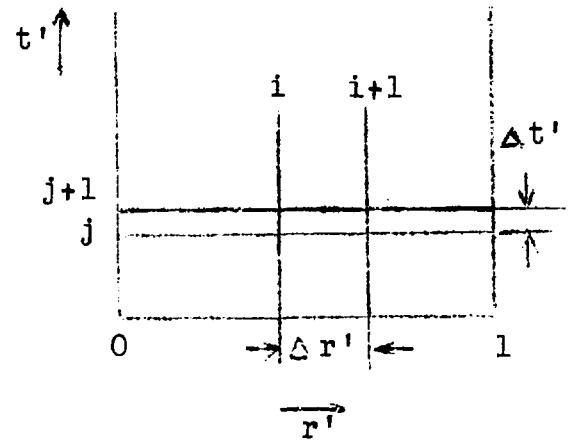
7. When the values of C calculated agree accurately with the guessed values, they may be assumed to be the correct ones for time t_{i+1}, and so a similar procedure may be undertaken for time t_{i+2}, and so on.

CONSTRUCTION OF THE FINITE DIFFERENCE EQUATIONS

When solving an equation such as (1):

$$Y_R \frac{\partial w}{\partial t'} = \left[\frac{\partial^2 w}{\partial r'^2} + \frac{2}{r'}\frac{\partial w}{\partial r'}\right]$$

with a finite difference method, the general technique is to construct a grid of rectangles of side $\Delta r'$ by $\Delta t'$, and use the value of w at the intersections of the grid to estimate the required partial derivatives

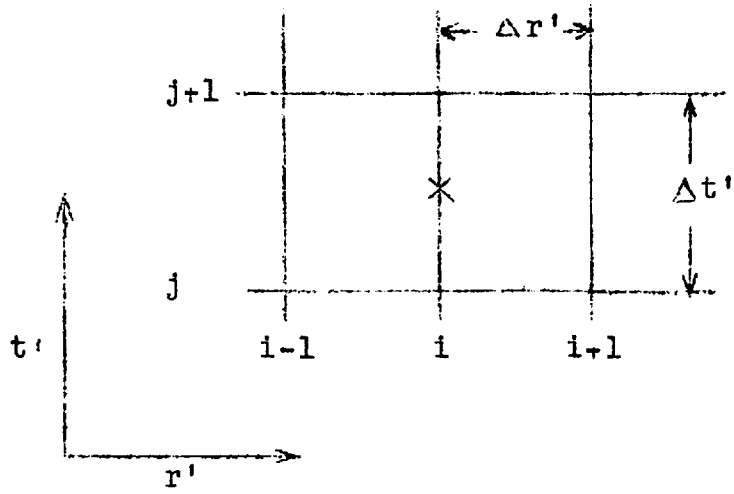


For example, an estimate of $\frac{\partial w}{\partial t'}$ for $r' = i\ (\Delta r')$, $t' = (j + \frac{1}{2})\Delta t'$ is seen to be $\frac{w_{i,j+1} - w_{i,j}}{t'}$. The terms of the left hand side could be estimated in a similar manner, and an equation relating values of w for various points of the grid, could then be said to be an approximation to equation (1), over a small region of the grid. Equivalent equations may be written for each point along a line of constant t. These equations may be used in two distinct manners (depending on how they were formulated) to compute new values of w for the next line of constant t: if each equation contains only one value of w that is not already known, the equations may be solved individually, and the technique is known as 'explicit'. If more than one unknown value of w appears in each equation, then they must of course be solved simultaneously, and the method is known as 'implicit'.

The merit of the explicit method is that, because simultaneous equations are not involved, it is fairly easy to carry out with hand computation. Its chief disadvantage, though, is that, in order for the solution to be stable, $\Delta t'/(\Delta r')^2$ must never exceed $\frac{1}{2}$. The implicit method, on the other hand has no such restrictions on it, and as a computer may be used to carry out the calculations,

simultaneous equations do not present a problem. It was not known whether or not it would be desirable to allow $\Delta t'$ to exceed $2(\Delta r')^2$, but on the chance that it would be, it was decided that use of the implicit method was advisable.

Consider a portion of the aforementioned grid:



Three adjacent values of w at constant t are needed to estimate $\partial^2 w/\partial r'^2$, and two values of w at constant r' are required for $\partial w/\partial t$ - so the six points shown above should be sufficient to write a finite difference equation. In order to make it of the correct form for the implicit method, it seems reasonable to compute the right hand side at j and at j+1 and average the values. The left hand side may be evaluated at i only. The equation so obtained may then be thought of as holding

for the point $(i, j+\frac{1}{2})$

$$\left(\frac{\partial w}{\partial r'}\right)_{i,j} = \frac{w_{i+1,j} - w_{i-1,j}}{2\Delta r'}, \left(\frac{\partial w}{\partial r'}\right)_{i,j+1} = \frac{w_{i+1,j+1} - w_{i-1,j+1}}{2\Delta r'}$$

and, since $r' = i\Delta r'$

$$\frac{2}{r'}\left(\frac{\partial w}{\partial r'}\right)_{i,j+\frac{1}{2}} = \frac{w_{i+1,j+1} + w_{i+1,j} - w_{i-1,j+1} - w_{i-1,j}}{2i(\Delta r')^2}$$

Similarly $\left(\frac{\partial^2 w}{\partial r'^2}\right)_{i,j+\frac{1}{2}}$

$$= \frac{w_{i-1,j+1} + w_{i-1,j+1} + w_{i+1,j} + w_{i-1,j} - 2w_{i,j+1} - 2w_{i,j}}{2(\Delta r')^2}$$

and, as noted previously $\left(\frac{\partial w}{\partial t}\right)_{i,j+\frac{1}{2}} = \frac{w_{i,j+1} - w_{i,j}}{\Delta t'}$

A finite difference equation representing diffusion in a crystal may now be written:

$$\frac{(\Delta r')^2}{\Delta t'} Y_R \left(w_{i,j+1} - w_{i,j}\right) = \left(\frac{1}{2} - \frac{1}{2i}\right)\left(w_{i-1,j+1} + w_{i-1,j}\right) - \left(w_{i,j+1} + w_{i,j}\right) + \left(\frac{1}{2} + \frac{1}{2i}\right)\left(w_{i+1,j+1} + w_{i+1,j}\right)$$

This equation may be used for all values of $j \geq 0$, and for values of i such that $0 < i < s$, where s is the total number of steps in crystal radius.

Consider the equation for i = 1:

$$\frac{(\Delta r')^2}{\Delta t'} Y_R \left(w_{1,j+1} - w_{1,j}\right) = -\left(w_{1,j+1} + w_{1,j}\right) + \left(w_{2,j+1} - w_{2,j}\right)$$

It is clear that this equation does not contain any

values of w_o.

Thus, one is faced with s - 1 equations containing S unknowns.

One more equation - for i = s may be obtained from the general form in the following manner:

For i = s, the general equation contains the fictitious points $w_{s+1,j}$ and $w_{s+1,j+1}$

Since $\left(\frac{\partial w}{\partial r'}\right)_1 = \frac{w_{s+1} - w_{s-1}}{2\Delta r'}$ (which will be defined as g)

one may say that $w_{s+1} = w_{s-1} - 2\Delta r'g$. When this value of w_{s+1} is substituted into the equation for i = s, it becomes:

$$\frac{(\Delta r')^2 Y_R}{\Delta t'}\left(w_{s,j+1} - w_{s,j}\right) = \left(w_{s-1,j+1} + w_{s-1,j}\right) - \left(w_{s,j+1} + w_{s,j}\right) + \left(\frac{s+1}{s}\right)\Delta r'\left(g_{j+1} + g_j\right)$$

One now has the complete set of s equations with which to determine the s new values of w. However, one extra unknown, g_{j+1} has been introduced, so that the new values of w are not yet completely determined.

$g = \left(\frac{\partial w}{\partial r'}\right)_1$ is of course equal to $\frac{T}{E}\frac{V_1 Y_R}{3X_R}\left[\frac{\partial^2 C}{\partial R'^2} + \frac{\alpha}{R'}\frac{\partial C}{\partial R'}\right]$ from equation (2), and so it may be seen to provide the link between equations (1) and (2).

For convenience, the set of equations may be written in matrix form.

Let $\underset{\sim}{A}$ be a square matrix of order s, such that:

$$\underset{\sim}{A} = \begin{matrix} -1 & +1 & 0 & 0 & \cdots & 0 \\ +1/4 & -1 & +3/4 & 0 & & \vdots \\ 0 & +1/3 & -1 & +2/3 & & \vdots \\ \vdots & & & & & \\ \vdots & & & & & 0 \\ 0 & \cdots & \cdots & \cdots & 0 & +1 \quad -1 \end{matrix}$$

And let $\underset{\sim}{B}$ be a vector with s elements of the form:

$$\underset{\sim}{B} = \begin{matrix} 0 \\ 0 \\ \vdots \\ \vdots \\ 0 \\ \left(\frac{s-1}{s}\right)\Delta r' \end{matrix}$$

Representing $w_{i,j+1}$ by w_i, and $w_{i,j}$ by $\dot{w}_i$, and defining Y as $Y \equiv \frac{(\Delta r')^2 Y_R}{\Delta t'}$, the set of equations may now be written:

$$Y\,(\underset{\sim}{w} - \dot{\underset{\sim}{w}}) = \underset{\sim}{A}\,(\underset{\sim}{w} + \dot{\underset{\sim}{w}}) + \underset{\sim}{B}\,(g + \dot{g})$$

$$\text{or} \quad 0 = (\underset{\sim}{A} - Y\underset{\sim}{I})\,\underset{\sim}{w} - (\underset{\sim}{A} + Y\underset{\sim}{I})\,\dot{\underset{\sim}{w}} + \underset{\sim}{B}\,(g + \dot{g})$$

$$\text{or} \quad 0 = \underset{\sim}{w} + (\underset{\sim}{A} - Y\underset{\sim}{I})^{-1}\,(\underset{\sim}{A} + Y\underset{\sim}{I})\,\dot{\underset{\sim}{w}} + (\underset{\sim}{A} - Y\underset{\sim}{I})^{-1}\,\underset{\sim}{B}\,(g+\dot{g})$$

And, letting $\underset{\sim}{C} = -(\underset{\sim}{A} - Y\underset{\sim}{I})^{-1}\,(\underset{\sim}{A} + Y\underset{\sim}{I})$, $\underset{\sim}{D}' = (\underset{\sim}{A} - Y\underset{\sim}{I})^{-1}\,\underset{\sim}{B}$

$$\underset{\sim}{w} = \underset{\sim}{C}\,\dot{\underset{\sim}{w}} - \underset{\sim}{D}'\,(g + \dot{g})$$

Considering for a moment the last term of this equation, one may separate it into vector and scalar parts:

$$(\underset{\sim}{A} - Y\underset{\sim}{I})^{-1} \begin{bmatrix} 0 \\ 0 \\ 0 \\ \cdot \\ \cdot \\ 0 \\ 1 \end{bmatrix} \quad \text{and} \quad \left(\frac{s+1}{s}\right)\Delta r' \ (g + \dot{g})$$

From equation (2):

$$\left(\frac{\partial w}{\partial r'}\right)_1 \equiv g = \frac{V_1 Y_R T}{3X_R E}\left[\frac{\partial^2 C}{\partial R'^2} + \frac{\alpha}{R'}\frac{\partial C}{\partial R'}\right]$$

Now if g_p is defined as $\left[\frac{\partial^2 C}{\partial R'^2} + \frac{\alpha}{R'}\frac{\partial C}{\partial R'}\right]\Delta R'^2$

(so that $g = \frac{V_1 Y_R}{3X_R}\frac{g_p T}{\Delta R'^2 E}$, the scalar part of the last term may be written: $\left(\frac{s+1}{s}\right)\Delta r' \frac{V_1 Y_R T}{3X_R R'^2 E}(g_p + \dot{g}_p)$

And defining $\left(\frac{s+1}{s}\right)\Delta r' \frac{V_1 Y_R T}{3X_R R'^2 E}$ as Z and $(\underset{\sim}{A} - Y\underset{\sim}{I})^{-1} \begin{bmatrix} 0 \\ 0 \\ 0 \\ \cdot \\ \cdot \\ 0 \\ 1 \end{bmatrix}$ Z as $\underset{\sim}{D}$, the final form of the finite difference equations becomes: $\underset{\sim}{w} = \underset{\sim}{C}\,\dot{\underset{\sim}{w}} - \underset{\sim}{D}\,(g_p + \dot{g}_p)$

The definition of g_p $\left(g_p \equiv \left[\frac{\partial^2 C}{\partial R'^2} + \frac{\alpha}{R'}\frac{\partial C}{\partial R'}\right]\Delta R'^2\right)$ has anticipated the next step, which is the expression of equation (2) in finite difference form.

The general equation follows at once from that written for equation (1), due to the obvious similarity of the two right hand sides

$$g_{pi} = \left(1 - \frac{\alpha}{2i}\right)C_{i-1} - 2C_i + \left(1 + \frac{\alpha}{2i}\right) C_{i+1}$$

When $\alpha = 2$, $\left(1 - \frac{\alpha}{2i}\right) = 0$ for $i = 1$, and so C_o is not needed to compute g_{p_1}. C_o may consequently be ignored during the calculations. If ten steps in pellet radius are used, this simplification results in a saving of about 10% in computing time and space. For this reason, it is tempting to see if it can be safely ignored even when α is not two.

The correct expression for g_{p_1} is $\left(1 - \frac{\alpha}{2}\right)C_o - 2C_1 + \left(1 + \frac{\alpha}{2}\right)C_2$. If $\beta\left(-C_1 + C_2\right)$ is used as an approximation to this, the error ϵ will be seen to be:

$\left(1 - \frac{\alpha}{2}\right) C_o + (\beta - 2)\, C_1 + \left(1 + \frac{\alpha}{2} - \beta\right) C_2$ or,

$\epsilon = \left(1 - \frac{\alpha}{2}\right)(C_o - C_1) + \left(1 + \frac{\alpha}{2} - \beta\right)(C_2 - C_1)$. Now since $\frac{\partial C}{\partial R'}$ is zero at the centre of the pellet, to a second approximation one may say that $C_2 - C_1 = -3(C_o - C_1)$ Accordingly, ϵ will be minimized if β is chosen so that

$\left(1 - \frac{\alpha}{2}\right) = 3\left(1 + \frac{\alpha}{2} - \beta\right)$. ie if $\beta = \frac{2 + 2\alpha}{3}$

(It will be seen that this leads to the expected value of 2 when $\alpha = 2$.) Two computer runs were carried out, one using this approximation and one using the correct expressions for g_{p1} and g_{po}. Since the results were virtually indistinguishable, the approximate form was adopted for use in all subsequent runs.

The equation for i = R (where R is the number of steps in pellet radius) is

$$g_{pR} = 2C_{R-1} - 2C_R + \left(2 + \frac{\alpha}{R}\right)\Delta R' \left(\frac{\partial C}{\partial R'}\right)_1$$

It will be seen later that there is no advantage to be gained from expressing the R equations in matrix form. However it is again worthwhile to consider the last term of the final equation:

$$\left(2 + \frac{\alpha}{R}\right)\Delta R' \left(\frac{\partial C}{\partial R'}\right)_1$$

From equation (3): $\left(\frac{\partial C}{\partial R'}\right)_1 = \frac{-V_o X_R}{(\alpha + 1)(1 - V_o)} \left(\frac{\partial C}{\partial l'}\right)$

And so if one lets $\frac{\partial C}{\partial l'} \equiv \frac{H}{\Delta l'}$, the last term becomes:

$$-\left(2 + \frac{\alpha}{R}\right) \frac{\Delta R'}{(\alpha + 1)} \frac{V_o X_R}{(1 - V_o)} \frac{H}{\Delta l'}$$

If X is defined as $-\left(2 + \frac{\alpha}{R}\right) \frac{\Delta R'}{(\alpha + 1)\Delta l'} \frac{X_R}{(1 - V_o)} V_o$, the

equation for i = R becomes $g_{pR} = 2C_{R-1} - 2C_R + XH$

As for the previous set of equations, one has R equations with which to find the R values of g_p - but again there is one extra unknown. This time it is the value of H. H, or $\left(\frac{\partial C}{\partial l'} \Delta l'\right)$ may easily be evaluated for each pellet by use of the finite difference approximation

$$\left(\frac{\partial C}{\partial l'}\right)_i = \frac{C_{i+1} - C_{i-1}}{2 \Delta l'}$$

This approximation corresponds to the assumption that, over a range of three adjacent points, the points may be fitted by an equation of the form $C = a_o + a_1 l' + a_2 l'^2$. Obviously a more sophisticated approximation would result from a higher order polynomial. But equally obviously, too many terms in the polynomial (i.e. the requirement that the curve fit too many points) will tend to reduce the accuracy of the approximation. In this case $C = a_o + a_1 l' + a_2 l'^2 + a_3 l'^3$ was used to give estimates of $\frac{\partial C}{\partial l'}$. The general form is

$$\left(\frac{\partial C}{\partial l'}\right)_i = \left(\frac{C_{i-2}}{12} - \frac{2C_{i-1}}{3} + \frac{2C_{i+1}}{3} - \frac{C_{i+2}}{12}\right) \frac{1}{\Delta l'}$$

The special formulae for the pellets near the ends of the bed will be given later.

If Q is the number of steps in bed length, then it is apparent that one has Q + 1 equations with which to determine the Q + 1 unknown values of H. Thus one has at last obtained a sufficient number of equations with which to compute the values of w(r', R', l'), g(R', l'), H(l') and C(R', l') at each new step in time, according to the method outlined previously. However, there are still a number of points to be considered before a successful programme may be written to solve this set of equations. They are set out under separate headings below.

Dimensionless Groups

Three dimensionless groups (X, Y and Z) have been defined, and it is worth while to examine each of these in turn.

r' = 1 at the surface of a crystal and, since there are s steps in crystal radius, $\Delta r' = \frac{1}{s}$. Similarly $\Delta R' = \frac{1}{R}$, $\Delta l' = \frac{1}{Q}$ and, recalling that $t' = \frac{t}{T}$, $\Delta t' = \frac{\Delta t}{T}$. One may now define T as being equal to Δt - so that $\Delta t' = 1$.

The three dimensionless groups

$$X \equiv -\left(2 + \frac{\alpha}{R}\right)\frac{\Delta R'}{\Delta l'}\frac{V_o}{(1 - V_o)}\frac{X_R}{(1 + \alpha)}$$

$$Y \equiv \frac{(\Delta r')^2}{\Delta t'} Y_R$$

$$Z \equiv \left(\frac{s+1}{s}\right)\frac{\Delta r' V_1 TY_R}{3(\Delta R')^2 EX_R}$$

may therefore be rewritten as follows:

$$X = -\left(2 + \frac{\alpha}{R}\right)\frac{V_o}{(1 - V_o)(1 + \alpha)}\frac{G}{R} X_R$$

$$Y = \frac{Y_R}{s^2}$$

$$Z = \frac{V_1}{3}\frac{(s + 1)}{s^2} R^2 \frac{TY_R}{EX_R}$$

Initial Conditions

Consider for a moment the initial conditions of the bed, as expressed for the finite difference equations. One may say that, at time = 0 all values of C and w are zero (and hence all values of g, H etc. are also zero) excluding only those of the pellet at the inlet to the bed. For this pellet, the value of the gas concentration at the surface is always that of the feed, so that $C_o = 1$. (Since the only link between conditions in the various pellets is the use of the gas concentration at their surfaces, this one fact is all that one will ever need to know about the zeroeth pellet.)

Special Formulae for the Computation of H_i

Various expressions were tried for the purpose of computing the values of H_i near the ends of the adsorber. One may infer from this that expressions finally chosen, although perhaps the best available, may still result in solutions for the end points of inferior quality to those for the interior points. Fortunately, the behaviour of the interior points does not appear to be seriously affected by these shortcomings.

Since C_o is always equal to unity, it follows that H_o must always be zero. These two facts are useful in that they suggest a method of computing H_1: one may stipulate that the cubic expression $C = a + bl' + cl'^2 + dl'^3$ shall have a slope of zero and a value of 1 at $l' = 0$, and that it shall pass through C_1 and C_2. If the derivative of this is then evaluated at the first pellet, H_1 is found to equal $-\frac{5}{4} + C_1 + \frac{C_2}{4}$.

For H_{Q-1}, it seems adequate to fit a cubic to the last four points in the bed. This yields the expression $\frac{C_{Q-3}}{6} - C_{Q-2} + \frac{C_{Q-1}}{2} + \frac{C_Q}{3}$ for H_{Q-1}. If this same curve is also used to obtain an expression for H_Q, $\left(\frac{C_{Q-3}}{3} + \frac{C_{Q-2}}{2} - 3C_{Q-1} + \frac{11}{6}C_Q \right)$ the values of H_Q are found to be

obviously inflated for some combinations of the programme parameters. The expression

$$H_Q = \frac{C_{Q-2}}{2} - 2C_{Q-1} + \frac{3C_Q}{2} ,$$

derived from fitting a quadratic to the last three points, was therefore tried instead, with much better results.

When one considers the physical system, it is apparent that C(l') is a monotonically decreasing function of l'. This means that $\left(\frac{\partial C}{\partial l'}\right)_i$, and therefore H_i must always be either zero or negative. It is obvious that H_1 will always fulfil these conditions - but equally obvious that H_2, as presently expressed, will not (when $C_1 = C_3 = C_4 = 0$ for instance). The same difficulty may arise for H_3, H_4 etc. In order to eliminate the chance of having H_i exceed 0, the following procedure has been adopted: H_i is computed by the standard formulae. If it exceeds zero, it is then recomputed according to the formula $H_i = \frac{C_{i+1} - C_{i-1}}{2}$, which will always give a non-positive value of H_i.

Methods for guessing a set of values of C

In the computational procedure outlined at the beginning of this chapter, it was said to be necessary

to guess a set of values of C from which an improved set could be calculated. The rate of convergence to the correct set (and, in fact, whether or not convergence occurs), is dependent upon the nature of the method adopted for making the guesses. Three basic methods were tried with a number of variations on each. The results of these investigations are described below. (Discussions of these methods will be facilitated by the use of plots showing the results of various iterations, with coordinates "(C_i) guessed" and "(C_i) computed".)

1. Simple Methods

The simplest method is to use the most recently computed value of $\underset{\sim}{C}$ as the next guess for $\underset{\sim}{C}$. This method was unstable (as anticipated), but a very slight modification proved successful for a wide range of programme parameters. The modified form was:

$$\underset{\sim}{C}_{\text{new guess}} = F\,\underset{\sim}{C}_{\text{computed}} + (1 - F)\,\underset{\sim}{C}_{\text{old guess}}, \text{ with}$$

values of F between $\frac{1}{2}$ and $\frac{3}{4}$.

However, it may be seen that if

$$\frac{(C_i)_n \text{ computed} - (C_i)_{n-1} \text{ computed}}{(C_i)_n \text{ guessed} - (C_i)_{n-1} \text{ guessed}} \text{ remains less than } \frac{F-2}{F}$$

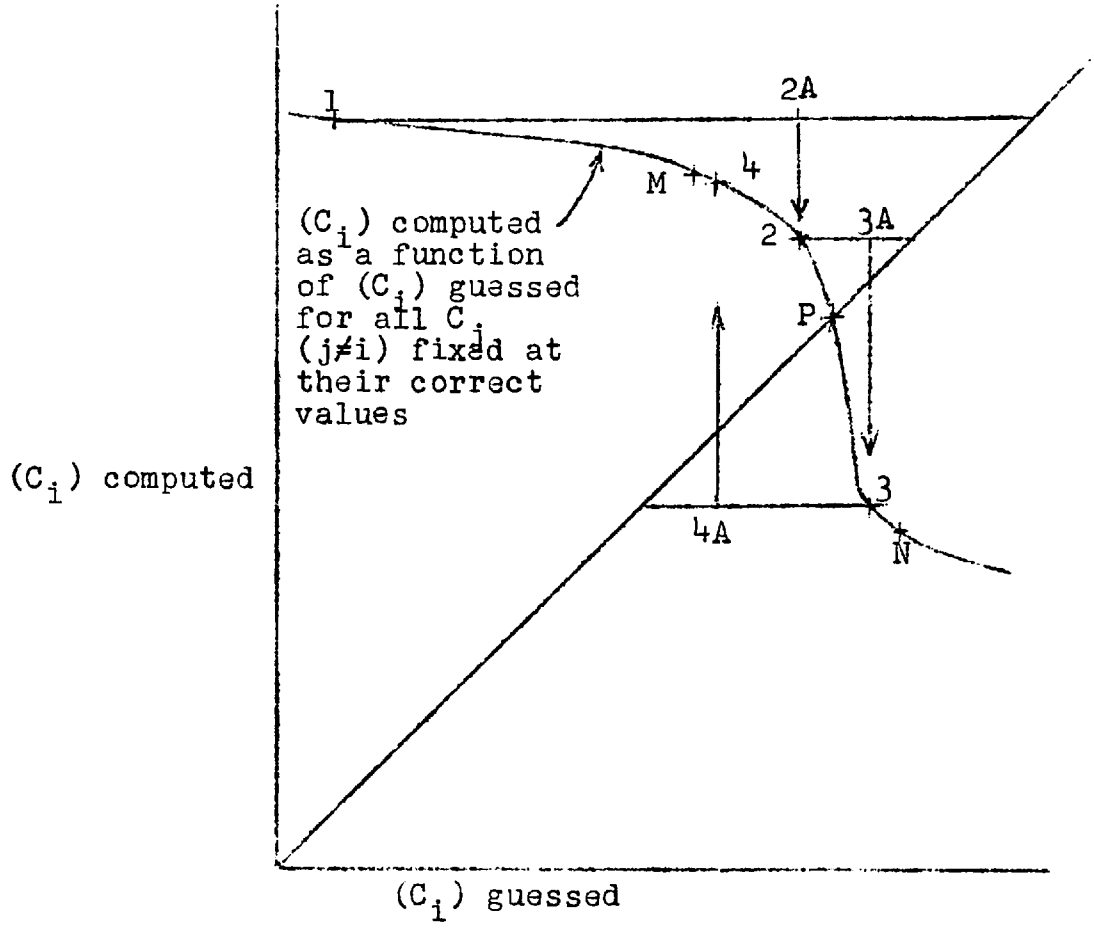
no matter how many iterations are carried out, this method will not lead to convergence. (This type of situation

is illustrated in Fig 3a.) It is apparent, however, that there is no lower limit on $\frac{F-2}{F}$ so if F is made smaller, it is possible to satisfy this necessary condition for convergence, but only at the price of a reduced rate of convergence. A further modification to this method was tried, in which the value of F_i used for any particular point, C_i, was adjusted in the light of the recent history of (C_i) computed and (C_i) guessed. But this proved to be inferior to a modified method of false position which will be described in detail later. First, though, another rejected method will be noted.

2. The Newton-Raphson Method

The simple method just outlined may be likened to the relaxation method of solving linear equations, since, for the purpose of making the next set of guesses, each of the Ci's is here considered to be a function of itself only. Use of the Newton- Raphson method for simultaneous non-linear equations allows one to use the true relationship between all the variables for the purpose of making the next set of guesses. A computer programme was written using this method, but it was soon found to require an excessive amount of computing time and was therefore abandoned.

Fig 3a

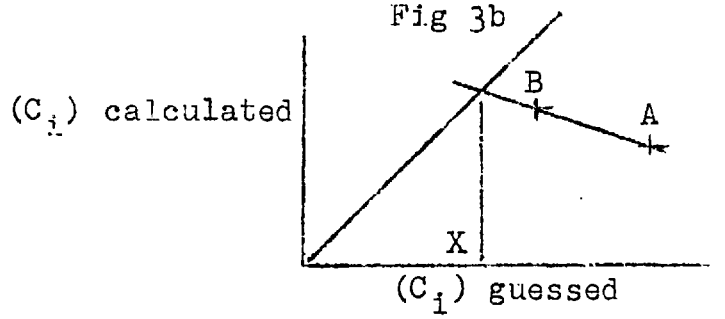


Point 1 represents the result of the first iteration and 2A indicates the value of C_i to be used for the next guess. Point 2 is the result of the second iteration, and so on. Instead of converging upon the correct value at P, the guesses will soon be oscillating between points M and N. (The assumption about all the other values of C_j was only made to make the points in the sketch lie on a smooth curve. In practice, they too will be adjusted at each iteration.)

3. The Method of False Position

The simplest method of false position joins the two most recent points, and uses as the next guess the coordinates of the intersection of this line with the diagonal passing through the origin. For example, in Fig 3b, if points A and B represent the results of the

Fig 3b

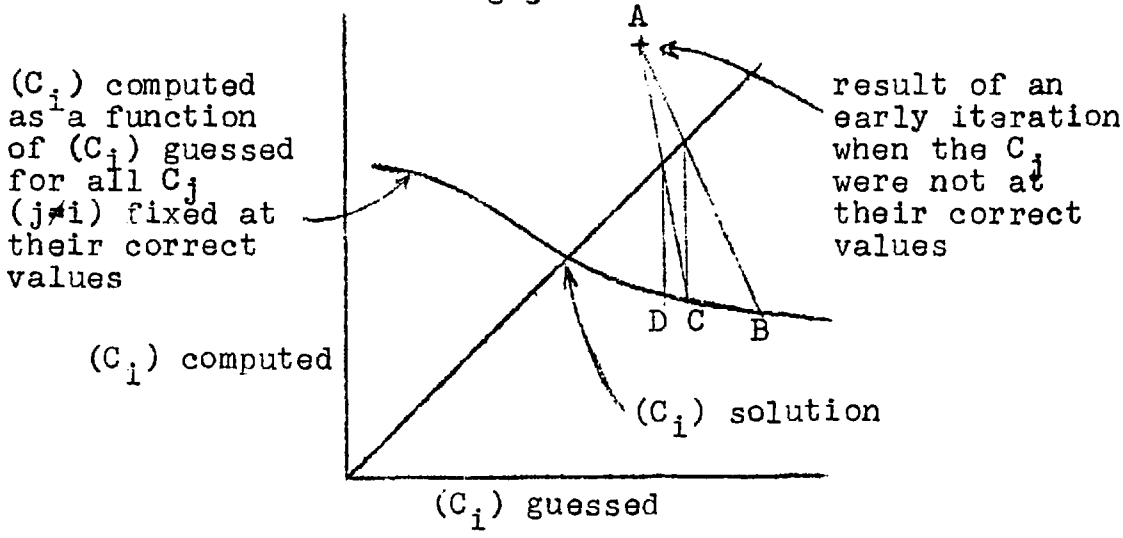


two most recent iterations, the next guess for C_i should be X.

A slight improvement on this method joins the most recent point above the diagonal with the most recent one below. (For a function of one variable, if the function is continuous, and if points above and below the diagonal can be found, then a solution exists and this method will converge to it.) However, as previously noted, it is only a crude approximation to say that each C_i is a function of itself only, and the presence of the other variables will lead to difficulties if it is not taken into account. Figure 3c illustrates the type of

situation that may arise due to this outside influence.

Fig 3c



It is apparent from this example that it will be impossible for (C_i) guessed to approach (C_i) solution if A is to the right of (C_i) solution, unless some modification to the standard method is made.

Various criteria were tried in order to enable the computer to recognise this type of situation, and to modify its action accordingly. The method finally adopted involves the computation of the ratio of the distance between the two most recent points, to the distance of the most recent one from the diagonal. If this ratio becomes too small, the next guess is made using the auxiliary form

$$(C_i)\ \text{guess} = F\ (C_i)\ \text{computed} + (1 - F)\ (C_i)\ \text{guessed}.$$

If the resultant point lies above the diagonal, it will be used to replace A as usual. If, however, it is below and to the left of A, the auxiliary form is used again. An equivalent technique is used for the case when the spurious point, "A", lies below the diagonal. This method, with a number of further refinements for the special cases that may be encountered, has proved very successful in obtaining rapid convergence in those cases where the simple method failed. For further details one may refer to the logic diagram of Fig 4, and to the computer programme itself in Appendix C.

Choice of Finite Difference Parameters

When a finite difference approximation is used to evaluate a derivative, it is essential that the interval between adjacent points be sufficiently small to ensure that the error introduced is not excessive. Two methods are available by which to decide how fine the subdivision should be: 1. Experimentally Starting with a relatively large interval it may be gradually decreased while note is taken of the effect on the results of the computation. Eventually, one hopes, further decrease in the size of the interval results in an unnecessary

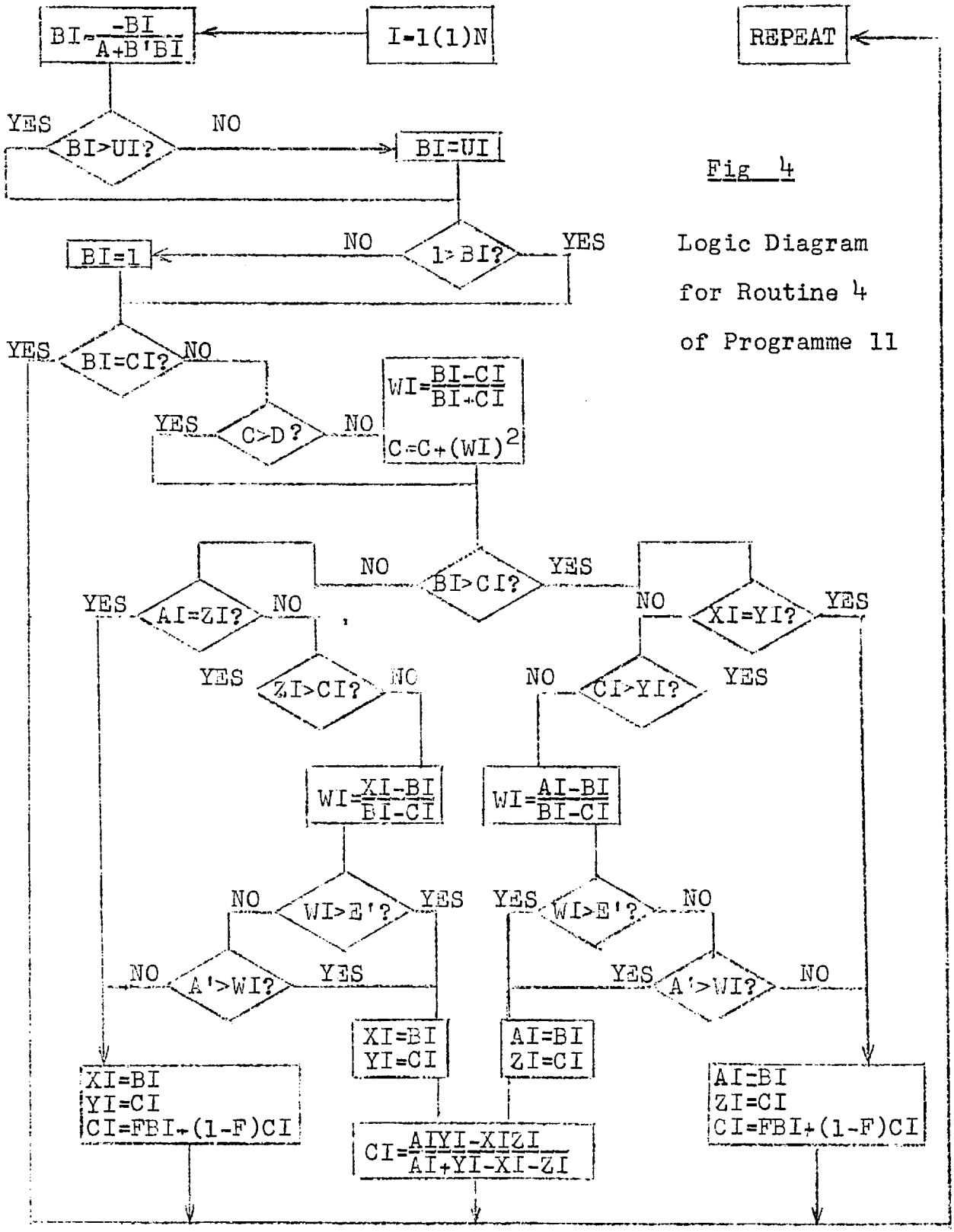


Fig 4

Logic Diagram for Routine 4 of Programme 11

improvement in accuracy. The largest interval consistent with sufficiently accurate results is then selected for further use. 2. Theoretically By examining the structure of the finite difference approximations it may be possible to predict the relation between the size of the interval and the accuracy of the result.

Either of these methods may be sufficient for use in simple cases, but in the present problem it was necessary to use a combination of these appraoches, using theoretical analysis at first and later evaluating some unknowns experimentally.

Theoretical Analysis

Intuition suggests, and computation confirms, that the various finite difference approximations will be put to their most severe test in the first pellet, at the first step in time. This is fortunate in that the simple initial conditions for this time step mean that it is relatively easy to examine the system in order to determine the various limiting factors.

Consider first the choice of s, the number of steps in crystal radius.

The finite difference approximations used in the crystal diffusion equation may be shown to be equivalent

to the assumption that the concentration profile may be fitted by a quadratic in the neighbourhood of the point at which the equation holds. If one considers the (limiting) case where w_s is non-zero while all the other w_i's are zero, (for any crystal), it is apparent that the quadratic that fits w_s, w_{s-1} and w_{s-2} will have a slope of $\frac{2w_s}{1/s}$ at i = s. And it is also apparent that the slope cannot exceed this value for any other physically possible possible values of w_{s-1} and w_{s-2}. Thus, if the physical value of the slope did exceed this limit, the finite difference approximation would be quite unable to represent it.

A practical method of seeing that this does not happen is to make sure that s is chosen to be sufficiently large so that $\frac{w_{s-1}}{w_s}$ always exceeds a minimum value.

The general matrix equation for any crystal has been written, $\underset{\sim}{w} = \underset{\sim}{C}\,\dot{\underset{\sim}{w}} - \underset{\sim}{D}\,(g + \dot{g})$. However, for the first step in time both $\dot{w}$ and $\dot{g}$ are zero, so the equation reduces to $\underset{\sim}{w}_1 = -\underset{\sim}{D}\,g_1$. Now $\underset{\sim}{D}$ was defined as $(\underset{\sim}{A} - Y\underset{\sim}{I})^{-1}\begin{bmatrix}0\\0\\\vdots\\1\end{bmatrix}$ Z and if the matrix algebra is carried out for several values of s (see Appendix D), the terms of $\underset{\sim}{D}$ may be seen to be of the form:

$D_i = -\frac{3Z}{2(s+1)Y}\,\frac{P_i(Y)}{P'_s(Y)}$, where $P_i(Y)$ and $P'_s(Y)$ are polynomials in Y of order (i-1) and (s-1) respectively. It follows immediately that $\frac{w_{s-1}}{w_s} = \frac{P_{s-1}(Y)}{P_s(Y)}$. As an example: For $s = 4$, $P_3 = 1 + 8/3Y + 4/3Y^2$ and $P_4 = 1 + 5Y + 6Y^2 + 2Y^3$ so $\frac{w_3}{w_4} = \frac{1 + 8/3Y + 4/3Y^2}{1 + 5Y + 6Y^2 + 2Y^3}$, and so for $Y = 1$, $\frac{w_3}{w_4} = .3571$

A set of curves of $\frac{w_{s-1}}{w_s}$ as a function of s and Y is presented in Appendix D (graph 1).

If one stipulates that $\frac{w_{s-1}}{w_s}$ shall always exceed a certain value, .5 for example, graph 2 in appendix D may be used to select a value of s for a particular value of $\frac{Y_F}{T}$. It is thus apparent that the value of T must be known before it is possible to choose s. (And the same dependence upon T will be found to apply for the choice of Q and R.)

It will be recalled that T arose from the finite difference approximation to $\frac{\partial w}{\partial t}$: $\frac{w_{t+\Delta t} - w_t}{\Delta t}$, (where T was later defined as equal to Δt). The derivation of this approximation from a Taylor series expansion of w(t) shows that the deviation from the true

value will increase with the square of T, but it gives no indication of the size of the deviation for any particular value of T. It will therefore be necessary to use the "experimental" method to determine T for any particular case.

In order to arrive at a method for choosing R, the number of divisions in pellet radius, consider the equations for one pellet, for R = 4, (with α = 2):

$$g_4 = -\ 2\,C_4 + 2\,C_3 + XH$$

$$g_3 = 4/3\,C_4 - 2\,C_3 + 2/3\,C_2$$

$$g_2 = 3/2\,C_3 - 2\,C_2 + 1/2\,C_1$$

$$g_1 = 2\,C_2 - 2\,C_1$$

From the previous section, for the first time step, $g_i = -\frac{w_{s_i}}{D_s}$. And so for a linear isotherm of the form

$$C = B'w_s,\ g_i = \frac{C_i}{B'D_s}.$$

If this last expression is used to eliminate the g's from the pellet equations, they may be seen to be identical in form to the set of crystal equations just discussed.

Where, $w \sim C$

$$Y \sim -(1/2B'D_s)$$

$$Zg \sim \frac{XH}{2}$$

Therefore, for example

$$\frac{C_3}{C_4} = \frac{1 - 8/3\ (1/2B'D_s) + 4/3\ (1/2B'D_s)^2}{1 - 5\ (1/2B'D_s) + 6\ (1/2B'D_s)^2 - 2\ (1/2B'D_s)^3}$$

It is apparent that $Y : s :: -1/2B'D_s : R$. Now since Y was defined as $\frac{Y_F}{s^2T}$, graph 2 was constructed with coordinates $\frac{Y_F}{T}$ and s. If this same graph is to be used for the determination of R, $\left(\frac{-R^2}{2B'D_s}\right)$ must be used as the ordinate. Examination of this group reveals that it may be simplified as follows:

Since $D_s = \frac{-3Z}{2(s+1)Y}\ \frac{P_s(Y)}{P'_s(Y)}$, $Z = \frac{(s+1)\ R^2 Y_F}{s^2 X_F}$

and $Y = \frac{Y_F}{s^2T}$, therefore $\frac{-R^2}{2B'D_s} = \frac{X_F}{3B'T}\ \frac{P'_s(Y)}{P_s(Y)}$

i.e. $\frac{Y_F}{T} : s :: \frac{X_F}{3B'T}\ \frac{P'_s(Y)}{P_s(Y)} : R.$

Further consideration of some of the relationships just noted leads to a method for the determination of Q.

We have seen that for a crystal $g = \frac{-w_s}{D_s} = \frac{2(s-1)\ Y\ w_s}{3Z\left(\frac{P_s(Y)}{P'_s(Y)}\right)}$

Accordingly, for a pellet $\frac{XH}{2} = \frac{2(R+1)(-1/2B'D_s)C_R}{3\left(\frac{P_R(-1/2B'D_s}{P'_R(-1/2B'D_s}\right)}$

Substituting the values of X, Y, Z and D_s, this expression reduces to the form: $C_R = \frac{-9}{4} \frac{T}{E} QH_1B' \frac{P_s(Y)}{P'_s(Y)} \frac{P_R(-1/2B'D_s)}{P'_R(-1/2B'D_s)}$

Values of $\frac{P_s(Y)}{P'_s(Y)}$ and $\frac{P_R(-1/2B'D_s)}{P'_R(-1/2B'D_s)}$ may be determined from graph 2; T, E and B' may be assumed to be fixed, so that the only variables are CR, Q and H_1. If one assumes that C_{2R} is almost zero for the first time step, then $H_1 = \frac{-5}{4} + C_R$.

If one now lets $k = \frac{9}{4} \frac{T}{E} B' \frac{P_s(Y)}{P'_s(Y)} \frac{P_R(-1/2B'D_s)}{P'_R(-1/2B'D_s)}$

then $C_R = - (\frac{-5}{4} + C_R) Q k$

or $Q = \frac{1}{k} \frac{C_R}{\frac{5}{4} - C_R}$

To facilitate selection of Q, one may construct a plot of k vs. C_R for a number of values of Q. (See graph 3, Appendix D.)

It will be noted that some of this discussion has been based on the use of a linear isotherm: $C = B'w_s$. However B' may equally well be taken to represent $\frac{C}{w_s}$ which is approximately $\left(\frac{dC}{dw}\right)_o$ for the small values with which we have been concerned.

It is now possible to describe a procedure for the determination of the finite difference parameters:

1. Do a computer run with values of Q R S and T which previous experience suggests are adequate to ensure a sufficiently accurate result. (The validity of this step will be tested in later ones.)
2. Perform a series of runs gradually increasing the value of T until the results begin to show signs of a loss of accuracy.
3. Select the largest value of T which gives an acceptable result.
4. Keeping Q R and T fixed, perform another series of runs in which S is systematically reduced, stopping again when the solution begins to deteriorate.
5. Select an acceptable value of s.

6, 7, 8 and 9. Repeat steps 4 and 5 first for R and then for Q.

10. One now has a set of values of the finite difference parameters which may be used in conjunction with the graphs of Appendix D to determine limiting values of $\frac{w_{s-1}}{w_s}$, $\frac{C_{R-1}}{C_R}$ and C_R.

If optimum values of these parameters are subsequently required for use with changed values of X_F, Y_F and/or E,

(but with the same isotherm), a simplified method can be used:

1. Determine T as before.
2. Use the limiting values of $\frac{w_{s-1}}{w_s}$, $\frac{C_{R-1}}{C_R}$ and C_R, with the graphs of Appendix D to determine Q R and S. (Because of the necessary approximations in the derivation of these graphs, it is probably advisable to use values of Q, R and S which are slightly larger than indicated above.)

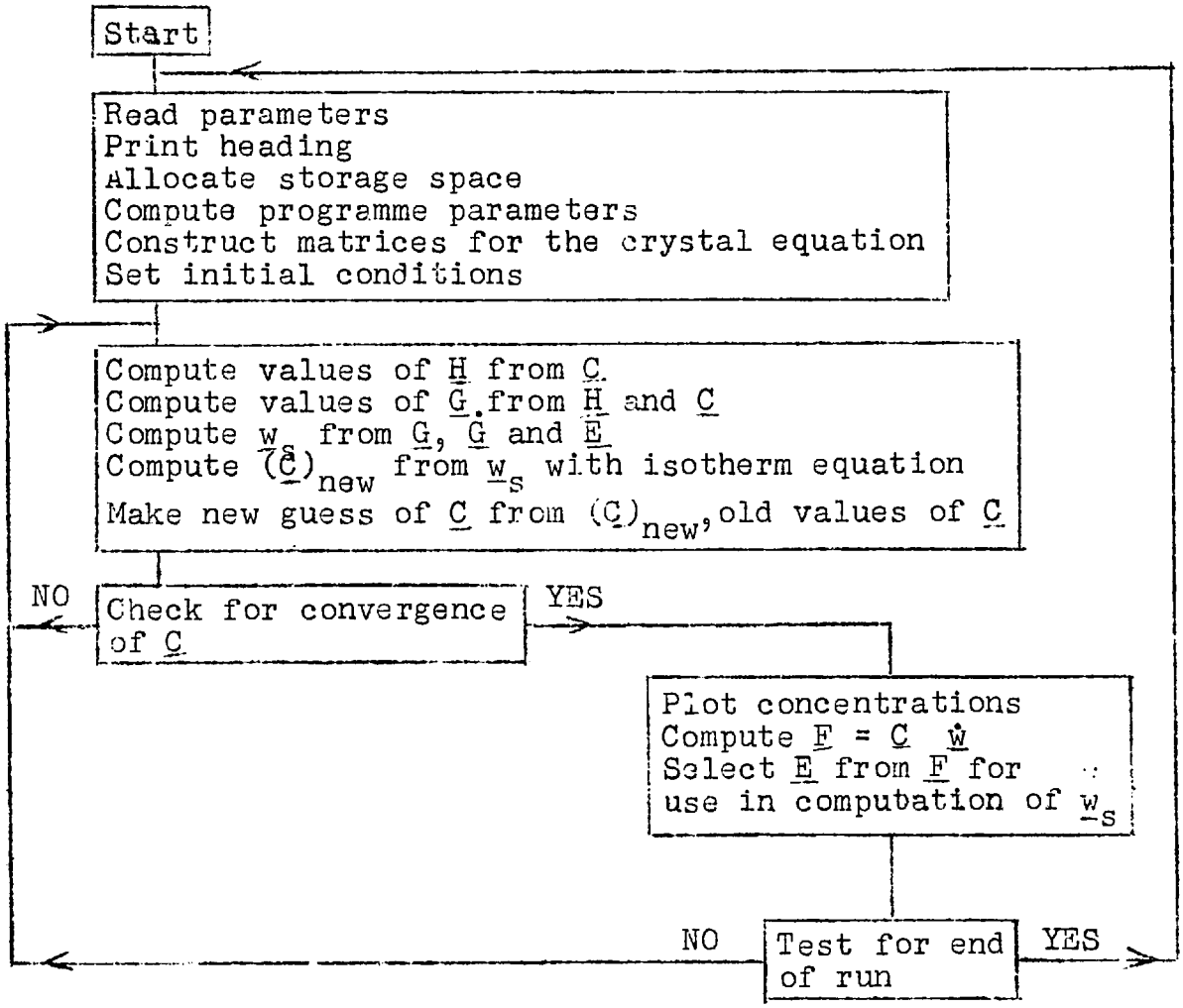
Although the work required to carry out these procedures is not great, the pressure of time made it expedient to forego the optimization of these parameters, and so all the computer runs reported in Chapter 8 were done with an unnecessarily finely divided space-time grid.

The computing procedure may now be described in some detail: (A logic diagram may also be seen in Fig. 5)

1. Assume that a new set of values of C(R', 1') has just been computed. The values of C(1, 1') are now plotted, as the only form of computer output. The plot is one of the form C(1, 1') against t for Q values of 1'.

Fig. 5

LOGIC DIAGRAM FOR COMPUTING PROCEDURE (PROGRAMME 11)



2. Immediately preceding the computation of the C's, a set of g's was computed. These are now used, together with other stored functions, to form: $\underset{\sim}{w} = \underset{\sim}{C}\,\dot{\underset{\sim}{w}} - \underset{\sim}{D}\,(g + \dot{g})$.

3. If one now assumes the time step to occur, then this value of $\underset{\sim}{w}$ becomes $\dot{\underset{\sim}{w}}$ and the g's become $\dot{g}$'s. $\underset{\sim}{F} \equiv \underset{\sim}{C}\,\dot{\underset{\sim}{w}}$ may be computed now and stored until it is needed again.

4. A set of values of $\underset{\sim}{H}$ is now computed, using the old values of $\underset{\sim}{C}$ as a guess for the new set of values.

5. These values of $\underset{\sim}{H}$, together with the guessed values of $\underset{\sim}{C}$ are used to compute a complete set of values of $\underset{\sim}{g}$. Any negative values of g are set equal to zero.

6. $\underset{\sim}{w} = \underset{\sim}{F} - \underset{\sim}{D}\,(g + \dot{g})$ is now computed - for values of w at the surface of the crystals only.

7. This set of values of w's is used to compute a new set of values of $\underset{\sim}{C}$ - using the isotherm equation. Any values of C which exceed one are made equal to one.

8. The new set of values of C is compared with the set of guessed values of C. If the change is excessive, the steps from 4. to 8. are repeated. Otherwise the whole process may be repeated from step 1. to 8.

Chapter 5

DESIGN OF EXPERIMENT

The purpose of this chapter is to show how the form of the mathematical model may be used to plan the experimental programme.

It is of course possible that a series of experiments devised to test a particular theory may overlook unforeseen phenomena that a less narrowly conceived programme might have revealed. However, it is fortunately the case that, although the mathematics of adsorption dynamics are complex, the processes involved are fairly well understood. As a result, it is unlikely that any new phenomena will be missed if the theoretical model is used to guide experimental design.

THE INFLUENCE OF THE ADSORPTION ISOTHERM

The object of this research is the study of the dynamic behaviour of a fixed-bed adsorber. The nature of the adsorption isotherm will of course have an influence on this, but since it relates to equilibrium rather than dynamic conditions, it is justifiable to omit it from the present study. This means that it is possible to perform

a complete series of experiments with one particular isotherm without incurring any loss of generality in conclusions drawn from this series.

THE DYNAMIC EQUATION

The following group of equations was derived in Chapter 3 to describe the dynamic behaviour of the adsorber:

$$Y_R \frac{\partial w}{\partial t'} = \frac{\partial^2 w}{\partial r'^2} + \frac{2}{r'}\left(\frac{\partial w}{\partial r'}\right)$$

$$\frac{3X_R E}{V_1 Y_R T}\left(\frac{\partial w}{\partial r'}\right)_1 = \frac{\partial^2 C}{\partial R'^2} + \frac{\alpha}{R'}\left(\frac{\partial C}{\partial R'}\right)$$

$$\frac{(\alpha + 1)(1 - V_o)}{V_o X_R}\left(\frac{\partial C}{\partial R'}\right)_1 = -\left(\frac{\partial C}{\partial 1'}\right)_1$$

If one represents the concentration of the gas leaving the adsorber by C' (i.e. C' = C for 1' = 1, R' = 1, and of course r' = 1), then C' may be seen to be a function of Y_R, t', $\frac{3X_R E}{V_1 Y_R T}$, and $\frac{(\alpha + 1)(1 - V_o)}{V_o X_R}$.

However, examination of these factors leads to a considerable simplification of the function.

Firstly, V_o, V_1 and α may all be treated as constants and consequently disregarded in the present discussions.

They are constant insofar as they are properties of the bed which are unaltered by changes in the operating conditions.

Secondly, if the values of X_R and Y_R are written out in full, it will be seen that the function takes the following form:

$$C' = \phi \left(\frac{s^2}{D_c T} , t' , \frac{S^2 D_c}{s^2 D_p} , \frac{D_p E}{S^2} \right)$$

Finally, one may note that t' was originally defined as $\frac{t}{T}$, where t is real time and T an arbitrary length of time introduced for the purpose of making t' dimensionless. The value of T will obviously have no effect on the value of the function, and consequently it is apparent that the first two groups on the right hand side must always appear in ratio i.e. $\frac{s^2}{D_c T} / \frac{t}{T}$, which reduces to $\frac{s^2}{D_c t}$. Thus $C' = \phi' \left(\frac{s^2}{D_c t} , \frac{S^2 D_c}{s^2 D_p} , \frac{D_p E}{S^2} \right)$

These three remaining dimensionless groups do not appear to be particularly meaningful, but since they are linearly independent they may be manipulated in the following manner to make the function more meaningful:

$$1 \Big/ \frac{s^2}{D_c t} \quad \frac{S^2 D_c}{s^2 D_p} \quad \frac{D_p E}{S^2} = \frac{t}{E} ,$$

$$\frac{s^2}{D_c t} \quad \frac{t}{E} = \frac{s^2}{D_c E} \quad ,$$

$$1 \quad / \quad \frac{D_p E}{S^2} = \frac{S^2}{D_p E}$$

The three new groups $\frac{S^2}{D_p E}$, $\frac{s^2}{D_c E}$ and $\frac{t}{E}$ may be seen to contain all the variables of the original groups, and since they are linearly independent, they may be adopted in place of the first set. Thus $C' = \phi\left(\frac{S^2}{D_p E} , \frac{s^2}{D_c E} , \frac{t}{E}\right)$. The bed residence time E is used as a measure of time for three quantities:

$\frac{S^2}{D_p}$, the pellet diffusion time constant

$\frac{S^2}{D_c}$, the crystal diffusion time constant

and t , real time.

The arguments of the above function suggest that a useful series of experiments would be one that measured C' as a function of $\frac{t}{E}$ for a range of values of $\frac{S^2}{D_p E}$ and $\frac{s^2}{D_c E}$. The worth of the mathematical model could then be assessed by observing whether or not the use of corresponding values of X, Y and E in the computer programme led to the same function of C' against $\frac{t}{E}$.

EXPERIMENTAL VARIATION OF THE DIMENSIONLESS GROUPS

Various methods are available to vary the two groups, but it will be remembered that change of temperature (or any other alteration to the isotherm) must be excluded.

E, the bed residence time is most easily varied, either by changing the gas flow rate or by the variation of effective bed length through the use of sample points along the axis of the adsorber (see Chapter 6). Runs were carried out using various flow rates but with all other conditions identical which verified that these two types of change were in fact equivalent. When this had been established, bed length variation was adopted as the principal means of varying E.

s, which represents crystal radius, will have a fixed value for a particular type of adsorbent due to the fact that crystal size distribution is characteristic of the adsorbent.

S, the pellet radius, can be easily varied by changing the size of pellet used in the bed. Two diameters were available, 1/8" and 1/16", which meant that S^2 could be varied by a factor of four.

D_c, the effective crystal diffusion coefficient, probably varies with temperature, but is otherwise constant. It may therefore be treated as such for the present series of experiments.

D_p, the effective pellet diffusion coefficient will presumably vary in direct proportion tc the free gas diffusion coefficient, which varies inversely with pressure. It should therefore be feasible to use a range of operating pressures as a means of achieving a range of values of D_p.

It is apparent that the only means of varying $\frac{S^2}{D_c E}$ is through variation of E. Fortunately, though, for any particular value of E, $\frac{S^2}{D_p E}$ may be made to assume a wide range of values by changes of pellet size or operating pressure. It is therefore possible to plan a set of operating conditions which will cover a fairly wide range of both the dimensionless groups upon which adsorber dynamics are thought to depend.

CHOICE OF OPERATING CONDITIONS

Temperature

Linde[10] has published isotherms for 0, 25, 50, 100, 200 and 300°C. Because of the necessity for water vapour

removal, which is difficult at high temperatures, 0°C was chosen as the most convenient of these temperatures at which to perform this series of experiments. (For similar reasons industrial CO_2 removal is liable to be carried out near to (but slightly above) the freezing point of water.)

Pressure

As previously noted, $\frac{S^2}{D_p E}$ can be changed by a factor of four by changing the pellet size. It was thought to be desirable to vary pressure by a factor of four as well to provide an opportunity to verify the equivalence of the two types of change. Because the non-ideality of the mixture laws increases with pressure, it is advantageous to avoid high operating pressures. Accordingly, the pressures chosen were 6.25 ata, 12.5 ata and 25 ata.

Concentration

Owing to the non-linearity of the isotherm, it is necessary to keep the partial pressure of the CO_2 in the feed at a fixed level even though the total pressure is changed from one run to another. 4.75 mm Hg (which corresponds to concentrations of 1000ppm, 500 ppm and 250 ppm respectively, at the chosen pressures) was chosen as a result of the following considerations:

1. The analyser used had three ranges: 0 - 100 ppm, 0 - 1000 ppm and 0 - 10,000 ppm. It was desirable to obtain the maximum possible deflection in order to enhance the accuracy of the results. The chosen concentrations may be seen to be best from this point of view.
2. These relatively low concentrations were chosen to avoid the effects of the heat of adsorption wave front that may arise for higher concentrations.
3. Finally, they are of the same order of magnitude as the concentration of CO_2 in atmospheric air (350 - 500 ppm).

Flow

For an industrial adsorber, economic considerations usually make it desirable to operate with a fairly high flow velocity. The maximum velocity is often dictated by the danger of particle attrition and may be computed from Ledoux's Criterion . The appropriate calculations were carried out for the various pressures (see appendix E), and the run needing the longest residence time was found to be that for 25 ata with the 1/16" diameter pellets. To give a margin for safety, double this time was chosen as the residence time for all the runs. Because E varies with pressure as well as flow, it was then necessary to calculate the flows required to maintain E at this con-

stant value for the various pressures. (See Appendix E).

Pellet Size

As previously noted, two pellet sizes were available; an identical series of experimental runs was carried out for each one.

The results of all these considerations are summarized in Table I.

TABLE I

OPERATING CONDITIONS FOR THE RUNS OF SERIES A

Feed temperature: $0^{\circ}C$

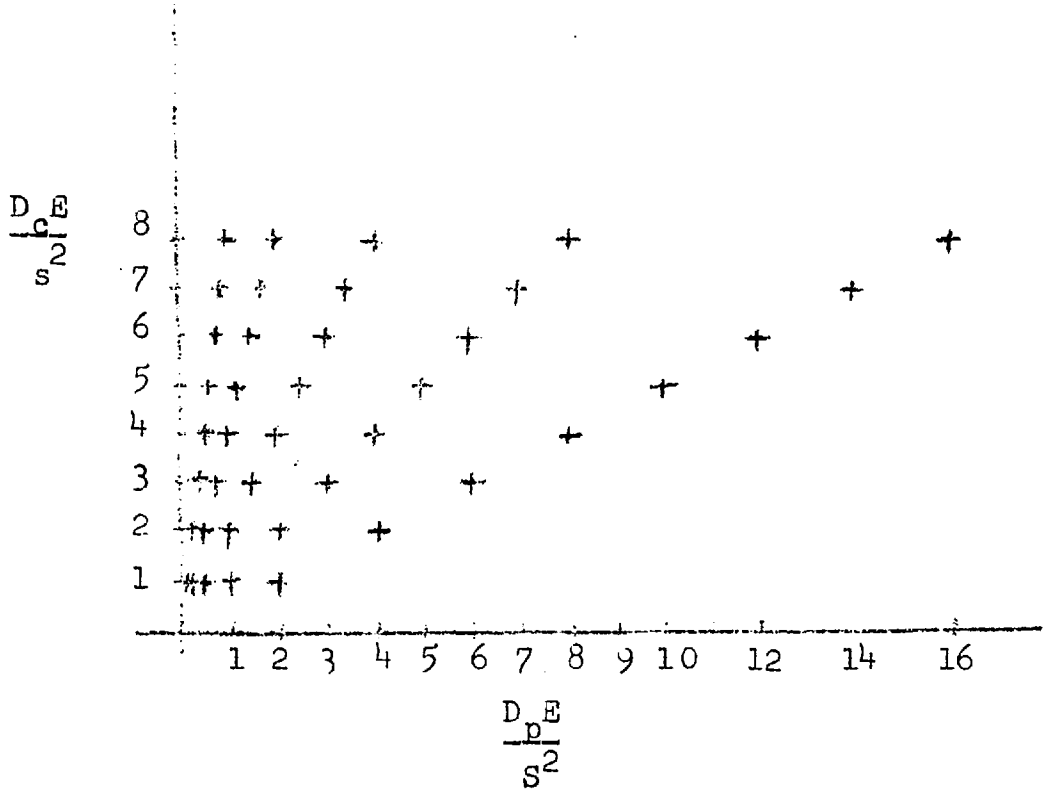
Partial pressure of CO_2 in feed: 4.75 mm Hg

Bed residence time: 7.5 seconds

Run number	1A	2A	3A	4A	5A	6A
Pressure, in ata	25	12	6.25	25	12.5	6.25
Feed concentration, in ppm of CO_2	250	500	1000	250	500	1000
Flow rate, in SCFM	15	7.5	3.75	15	7.5	3.75
Pellet diameter, in inches	1/8	1/8	1/8	1/16	1/16	1/16
$\frac{(S^2/D_pE)}{(S^2/D_pE)_{6A}}$	16	8	4	4	2	1

The residence time referred to above is for the whole bed, but because of the use of multiple sample points, each run will yield breakthrough data for eight residence times, ranging from .9375 seconds to 7.5 seconds in steps of .9375 seconds. Fig 6 shows the range of values of $\frac{D_n E}{s^2}$ and $\frac{D_c E}{s^2}$ covered by this series of six runs.

Fig. 6



(It should be noted that the numbers along the coordinate axis represent ratios rather than the actual numerical value of the dimensionless groups.)

In addition to the six runs of Series A, it was necessary to perform six more runs (Series B) in order to test reproducibility and the concept of residence time, and to determine an effective adsorption isotherm. The desired conditions for the runs of Series B are summarized in Table 2.

TABLE 2

DESIRED CONDITIONS FOR THE RUNS OF SERIES B

Run number	Pellet diameter in inches	Pressure in ata	Feed concentration in parts per million	Flow rate in SCFM
1B	1/16	6.25	1000	3.75
2B	1/16	6.25	1000	3.75
3B	1/16	6.25	1000	5.0
4B	1/16	6.25	1000	7.5
5B	1/16	6.25	500	7.5
6B	1/16	6.25	250	7.5

Reproducibility

It will be seen from this table that the conditions for runs 1B and 2B are identical to those for 6A. The

results of these three runs should therefore provide an indication of the degree of reproducibility achieved. Of all the runs of Series A, number six was chosen for this test because of its small value of S^2/D_p, which should result in the most easily compared breakthrough curves. (In fact, 6A was used as the basis for all the runs of Series B.)

Residence Time

Runs 3B and 4B differ from 6A only in the gas flow rates. Residence times for some of the bed lengths of these runs are shown in Table 3.

TABLE 3

RESIDENCE TIMES FOR SOME INDIVIDUAL POINTS FOR RUNS 6A, 3B, 4B

Run number	Residence time for complete adsorber in seconds	Residence time for individual points in seconds					
		1	2	3	4	5	6
6A	7.5	.9375	1.875	2.8125			
3B	5.625		1.40625		2.8125		
4B	3.75		.9375	1.40625	1.875		2.8125

It is clear from this table that a number of breakthrough curves for points with identical residence times (but with different gas flow rates) should be available for comparison.

Determination of Isotherm

It has been mentioned earlier that Linde has published some isotherms for CO_2 on molecular sieve 5A, and it was originally intended that some of these data would be used for computation. It became apparent, however, from a preliminary study of experimental results, that the "effective isotherm" of the adsorbent in use was significantly different from that of Linde. This was not entirely surprising, in view of the phenomenon of semipermanent water adsorption observed by Dworjanyn[5b], and from the marked dissimilarity between the isotherm determined by Chandrasekharan[2c], and the corresponding Linde data. Dworjanyn observed that the nature of the reactivation process seriously affects the degree of desorption obtained, but Chandrasekharan's results indicate that it is possible to obtain a reproducible degree of desorption through the use of a standard procedure for reactivation. Consequently, it is essential that any method adopted for the determination of an isotherm should

employ a regeneration technique identical to that used for the adsorber. A method was therefore devised which enabled an isotherm for the adsorbent actually in the adsorber to be determined from the results of a number of experimental runs, an approach which should yield a good approximation to the "effective isotherm".

This method can only be used if a "constant-pattern" adsorption wave front forms during a run. This will, in general, occur if two conditions are met: (a) the isotherm must be of the "favourable" type - i.e. concave to the gas concentration axis. (b) The adsorber must be long enough to allow the constant pattern to become properly established. The first condition is definitely satisfied for the CO_2-molecular sieve system, but the second one will only be satisfied under certain conditions. It is possible to obtain these conditions for the 1/16" diameter pellets, and it was for these that the isotherm was measured.

If a constant pattern wavefront does form it will be fairly easy to measure its velocity as it passes through the bed. From this, and from physical data on the adsorbent, one may calculate the weight of adsorbent saturated in a given time. And from the gas flow rate and feed composition, one may calculate the weight of

CO_2 causing this saturation. The ratio of these weights gives the value of q corresponding to the partial pressure of CO_2 in the feed, p. Thus one experimental run yields a single point on the effective isotherm, so the procedure must be repeated for a number of values of p if the shape of the isotherm is to be determined.

Owing to lack of time, only three points were determined by this method, but, as will be evident later, they appear to have given a fairly good basis for an isotherm. The part of the isotherm required was that for values of p less than 4.75 mm Hg. Accordingly, the largest value used was 4.75 mm Hg. (Run 4B). The other two runs (5B and 6B) used concentrations of one half and one quarter of this respectively.

The results of all twelve runs are reported in Chapter 7.

Chapter 6

EXPERIMENTAL APPARATUS AND ITS OPERATION

DESCRIPTION OF APPARATUS

The apparatus consists essentially of a vessel to contain the adsorbent, with provision for the analysis of the effluent, and a system to provide a flow of air/CO_2 mixture through this vessel under various conditions.

The Adsorber

The experimental adsorber was made from a piece of $3\frac{1}{2}$" SCH 80 SD TUBE made of EN 58B stainless steel, about four feet long. It was closed at the bottom end and had a screw plug fitted at the top, which was used to fill the vessel with adsorbent. A piece of fine wire gauze, supported by heavy wire gauze, was fixed across the bottom of the tube to support the adsorbent pellets, and $\frac{1}{4}$" i.d. process lines entered through the ends of the vessel. The diameter of the vessel was arrived at by consideration of the capacity of the compressor, and the maximum allowable gas velocity, based upon Ledoux's Criterion (which may be seen in Appendix E).

To observe the dynamics of the adsorption process inside the vessel, ten samples of the process gas were taken from equally spaced points along its length. The analyses of these samples yielded a fairly complete pattern of gas concentration as a function of distance from the inlet and time.

It may be noted here that because longitudinal dispersion can be neglected, the concentration vs. time curve for each of these points is also a breakthrough curve for an adsorber with the corresponding length.

Ten thermocouples were inserted through the wall of the vessel at positions corresponding to the sample points. These were used to obtain temperature profiles of the bed, during both operation and regeneration.

Industrial adsorbers which are thermally regenerated are usually heated by blowing gas first through a heater and then through the vessel (usually in the opposite sense to the process flow). In this case it was found to be more practical to heat the vessel directly using electrical heating tape. Two "Hotfoil" tapes, each eighteen feet long and one inch wide were wrapped helically around the vessel. Roughly three quarters of the surface of the vessel was covered by tape, and the heating achieved was correspondingly uniform. The vessel was

purged with a small flow of CO_2 free, dry air, after it had been kept at about 200°C for about six hours. When purging is complete, the CO_2 concentration in the effluent is usually about 50 ppm, but because of the high temperature the CO_2 concentration in the solid is virtually nil.

The Air Supply System (See Fig. 7)

The system that supplied air to the adsorber was made up of four main elements:

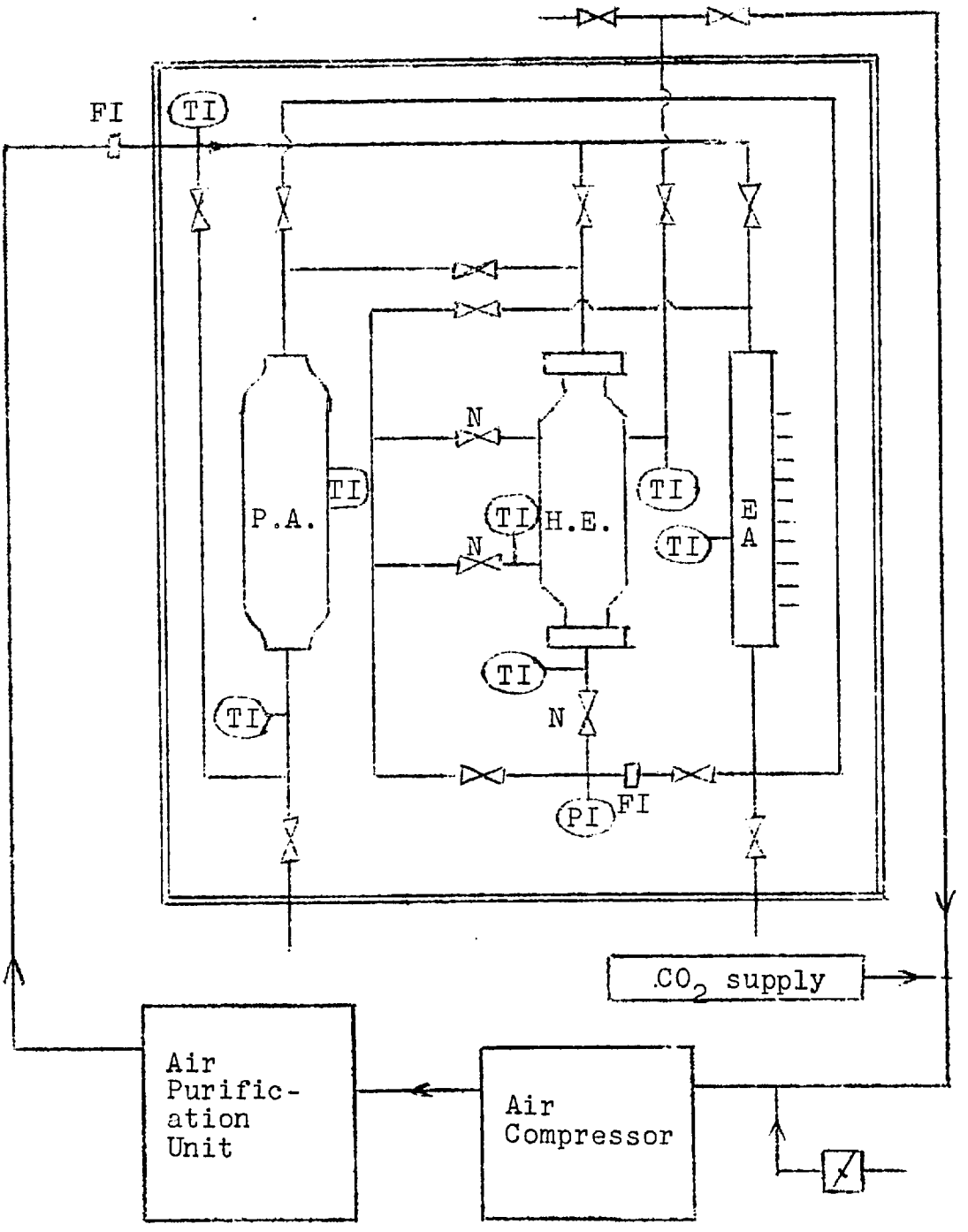
The compressor This was a four stage reciprocating compressor, water cooled and driven by a D.C. motor. It was rated at 280 lbs/hr of air at up to 4000 psig.

The purification unit The air leaving the compressor contained water vapour and oil vapour, as well as CO_2. The oil was removed by a small bed of activated alumina[11] , and the water by two dryers filled with Mobilbead R[12] which could be reactivated independently. Mobilbead R was chosen because it does not adsorb CO_2 while adequately removing water - to a dewpoint of -60°C.

The heat exchanger A wound tube high pressure heat exchanger was installed in such a way that the Joule-Thompson effect of the air was sufficient to attain the coldest temperature required.

Fig 7

Air Supply System



P.A. : preadsorber E.A. : experimental adsorber
H.E. : heat exchanger

The pre-adsorber This was a high pressure adsorber filled with molecular sieve adsorbent which was used to provide CO_2-free air while thermal equilibrium was being achieved before the start of an experimental run. In order to start a run, it was merely taken off-line. The dryers and the pre-adsorber were reactivated in much the same manner as the experimental adsorber.

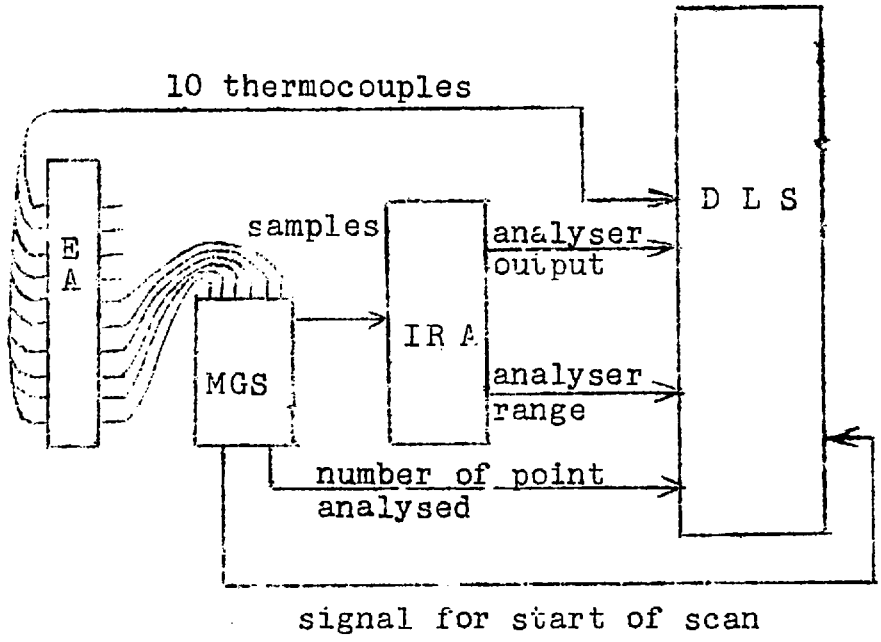
The two adsorbers, the heat exchanger and all their interconnecting pipework are enclosed in a box, filled with the finely powdered insulant, "Perlox 100". This was thought to be the most practical means of reducing heat leak, both during an experimental run, and for reactivation. A disadvantage, though, is that it cannot be easily removed to facilitate more rapid cooling after reactivation.

Sample Analysis System (See Fig. 8)

Although the adsorber is provided with ten sample points, it is not economic to provide more than one analyser to analyse these samples. Fortunately, because of the relatively slow rate of change of concentration with time for most conditions, it is feasible to analyse each sample intermittently, and so enable a number of points to be effectively observed by one analyser.

Fig. 8

SAMPLE ANALYSIS SYSTEM



E A : experimental adsorber

M G S : motorized gas switch

I R A : infra red analyser

D L S : data logging system

Under most conditions, it was practical to analyse one point per minute.

A motorized gas switch was purchased which was capable of sampling up to six points in cyclic succession. The wave front nature of the adsorption phenomenon means that for a long period of time only the first few points in the bed are of interest, as the rest remain virtually CO_2-free. Thus, initially, the points sampled could be 0, 1, 2, 3, 4 and 5. Later, when the concentration front has reached point 5, say, point 1 could probably be disconnected and moved to point 6 without a serious loss of information. This procedure may be repeated for the remaining points, so that each one is observed, at intervals of six minutes, during its period of maximum interest. This system means that it is not necessary to do more than one run for each set of operating conditions.

The samples selected by the motorized gas switch are analysed in an infra-red analyser which operates continuously. It has three ranges: 0-100 ppm, 0-1000 ppm and 0-10,000 ppm. The output voltage (2 to 10 mv) is recorded by a digital data logging system on seven hole paper tape. The temperature profile of the adsorber, as given by the ten thermocouples, is also recorded together

with two digits, one of which indicates which point is being sampled and the other the range of the analyser. A "sentence", which is recorded once every minute on command from the motorized gas switch might look like this:

120ØØ121ØØ... ...128ØØ129ØØ346ØØ3ØØ2NL

ten thermocouple outputs in volts x 10^{-3}

Analyser Output

Analyser Range

Number of point sampled

Ø denotes a "space" character

NL denotes a "new line" character

The thermocouple readings can be easily converted to temperatures knowing the temperature of the fixed junction and the calibration of the thermocouple.

The analyser output may be converted to ppm CO_2 knowing the zero and span outputs, and the fact that range 2 corresponds to 0-1000 ppm.

These calculations are in fact performed by two computer programmes, one for the analyser and the other for the temperatures.

OPERATING CONDITIONS

Five variables define the conditions of a run: pressure, temperature, flow, feed concentration and

pellet radius. For runs to be reproducible it is essential that all these be kept as nearly constant as possible for the duration of a run. To facilitate meaningful computation, the variables must be accurately measured. Only pellet radius leaves little to be desired in both respects.

The first three variables, pressure, temperature and flow, are functionally related by the laws of fluid dynamics. The general method, therefore, was to keep the pressures constant, allow the system to reach thermal equilibrium and thus ensure that the flow would stay constant also.

The flow of air may be directed through different paths, according to the experimental conditions desired, but in general it passes through three expansion valves in series:

An automatic pressure controlling valve was installed immediately following the purification unit. This was used to maintain a constant downstream pressure of, say, 200 ata.

A needle valve which was situated between the exchanger and the adsorber was used to drop the pressure to the level required in the adsorber.

Finally, another needle valve downstream of the adsorber reduced the pressure to near atmospheric.

Unfortunately, the compressor was subject to minor fluctuations in throughput. The system was therefore not without external disturbances from this quarter. The automatic pressure controlling valve was intended to reduce the magnitude of the fluctuations, and this it did admirably, but it probably did allow a variation of ± 2% in the downstream pressure. This variation was damped by the system to an extent which varied with the particular combination of pressures, temperatures and flow used.

Variations in temperature arose from three sources:

1. The fact that the system had not quite reached thermal equilibrium was reflected by a continuous change of temperature in the form on an exponential decay.
2. The variations in pressure caused slight variations of temperature by virtue of the Joule-Thompson effect.
3. The heat of adsorption phenomenon must lead to a temperature wave front associated with the concentration wave front.

The first of these was by far the most important: in a typical run the total change in temperature over a period of ten hours was three degrees centigrade. The fluctuations due to pressure changes were of the order of half a degree. It was impossible to detect any temperature change associated with the concentration wave front.

The measurement of flows was not as precise as that of pressures and temperatures, but it is likely that the percentage variation of flow was of the same order of magnitude.

The pressures were measured on three 0-350 atm. and one 0-400 psig. Bourdon gauges. The high pressure gauges were calibrated against a new standard gauge - probably to an accuracy of ± 1 atm. The low pressure gauge, which was used on the experimental adsorber, was calibrated on a dead weight tester, to an accuracy of ± 2 psig.

The thermocouples used were supposed to be accurate to ± 3°C (.16 mv) over the range -200°C to +400°C. However, the good agreement between the ten thermocouples observed under ambient conditions suggested that this error was too liberal: ± 1% of the output voltage seems more reasonable over the range covered in these experiments. This corresponds to an error of ± 2°C for the runs at zero °C. The temperature of the fixed junction (an oil bath in a dewar flask at room temperature) was measured with a mercury in glass thermometer with a range of 0 to 30°C. It was checked against another one which had been calibrated in ice and boiling water. It is not thought that the measurement of the cold junction temperature introduced a significant error.

A Foxboro high pressure d/p cell and a range of orifices of the same make were used to measure the flow rate of the air/CO_2 mixture. Care was taken in the piping layout to ensure a sufficient run of straight pipe upstream of the orifices to conform to the British Standards. However, because of the relatively large flows involved, it was not practical to calibrate the flowmeter. It was therefore necessary to use the value of the flow as computed from the manufacturer's data sheets. They suggested that the accuracy in these circumstances would be about ± 5%

When atmospheric air is used, without any additional CO_2, the variations in inlet CO_2 concentration during a run are about ± 5%. This performance was only achieved after a special air intake line for the compressor had been constructed to allow air to be drawn directly from out-doors. The percentage variation is of course unchanged when the recycle is in use, but decreases markedly when CO_2 is added to the air.

The data gathered in this experiment consist of a surface of CO_2 concentration in the adsorber as a function of time and distance. The distance between sample points in the adsorber is probably accurate to about ±.2% of its length. The measurement of time (by the motorized

gas switch) is probably even better than this. The accuracy of the analyser is said to be ± 1% of full scale so that for a feed of 400 ppm, and for a reading representing 50% saturation (200 ppm) the accuracy of the reading will only be ± 5%. However this may be unduly pessimistic: observations on the fluctuations in output observed when zeroing and spanning the analyser suggest that ± 2% of the output is not an unrealistic figure.

Chapter 7

EXPERIMENTAL RESULTS

A total of twenty one experimental runs were carried out under various conditions. Nine of these had to be discarded for a variety of reasons associated with the development of equipment and techniques. The remaining twelve are reported herein. Both plots and tables of the concentrations histories are contained in Appendix F. These were produced by processing the data tape on the Atlas Computer. The computer programmes are included in Appendix C.

No attempt was made to smooth the data, as it was felt that this mode of presentation gave a clear picture of the shape of the curves while also giving an indication of the precision of measurement. Tables 1 and 2 in Chapter 5 presented the desired experimental conditions for the runs of series A and B. Table 4, below, summarizes the conditions actually achieved. It will be noted that both pressure and flow rate correspond exactly with the desired conditions. Unfortunately, this is less an indication of extremely accurate control than a reflection of the fact that these quantities were not recorded sufficiently

often to enable mean values to be calculated. Deviations from these values were quite small, seldom exceeding 3%.

Table 4

EXPERIMENTAL CONDITIONS FOR THE RUNS OF SERIES A AND B

Run No	Pellet diameter in inches	Pressure in ata	Temperature in °C	Feed concentration in ppm of CO_2	Flow rate in SCFM
1A	1/8	25	1.4	249	15
2A	"	12.5	.8	493	7.5
3A	"	6.25	-2.1	998	3.75
4A	1/16	25	1.2	245	15
5A	"	12.5	-.6	499	7.5
6A	"	6.25	-1.5	998	3.75
1B	"	"	.7	996	3.75
2B	"	"	1.7	999	3.75
3B	"	"	-.3	1010	5
4B	"	"	-2.3	1004	7.5
5B	"	"	.9	501	7.5
6B	"	"	1.3	253	7.5

Conclusions drawn from consideration of the results of various groups of these runs are presented below.

Reproducibility

Runs 6A, 1B and 2B were carried out with almost identical operating conditions, with the first and last separated by a period of over three months. The similarity of the results is therefore not merely evidence of reproducibility, but also of long term stability of the system. There is no evidence that the shape of the effective isotherm has altered, since the slight differences in experimental conditions seem adequate to explain the differences in the results. If the time at which point number 4 reaches 5% of the feed composition is used as a means of comparing the results, all three runs are seen to be clustered within less than 2% of the mean.

Residence Time

Runs 6A, 3B and 4B were performed with all conditions the same, except for flow rate. The purpose of these runs was to try to establish whether flow rate and bed length were individually significant, or whether the ratio of the two quantities, the residence time, was sufficient to describe the influence of both variables.

The results of these runs are only slightly less consistent than those of the reproducibility runs, and

because the variations do not appear to be systematic, the use of the concept of residence time seems to be justified. Table 5 lists the times at which the gas concentrations reached 50% of the feed, for the points noted in Table 3.

Table 5

EFFECTS OF DIFFERENT GAS FLOW RATES ON POINTS WITH EQUAL RESIDENCE TIMES

Run Number	6A	3B	4B
Gas flow rate in SCFM	3.75	5.0	7.5
Residence time in seconds	Sample point number, and time (in minutes) at which concentration reached 50% of feed		
.9375	pt 1 86		pt 2 33
1.40625		pt 2 239	pt 3 236
1.875	pt 2 325		pt 4 327
2.8125	pt 3 505	pt 4 508	pt 6 509

Determination of Isotherm

Using Dworjanyn's[5H] data for the bulk density of packed molecular sieve pellets, the weight of adsorbent

between two adjacent sample points was calculated to be 1.25 pounds. The time interval between the arrival of the concentration wave at one sample point and its arrival at the next one was calculated by measuring this Δt for several concentration levels (15%, 50% and 85%), and for several sections of the cclumn. The results of these measurements confirmed the establishment of a constant-pattern wave (and also, incidentally, the uniformity of the gas flow rate). Mean values of these time intervals, for Runs 4B, 5B and 6B are recorded in Table 6, together with calculated values of p and q.

Table 6

DATA FROM RUNS 4B, 5B AND 6B FOR THE DETERMINATION OF POINTS ON THE EFFECTIVE ISOTHERM

Run number	Feed concentration in ppm of CO_2	p in mm Hg	time interval in minutes	weight of CO_2 in pounds	q wt %
4B	1004	4.77	87.2	.0762	6.07
5B	501	2.38	130.4	.0569	4.54
6B	253	1.20	167.5	.0369	2.94

It is apparent that these points cannot be usefully fitted with a straight line, so some sort of a non-linear expression must be used. It is, of course, possible to obtain a perfect fit of this small amount of data with a variety of three parameter equations. However, not only might this result in an unrealistically deformed curve, but it would yield no information about the relative merit of the various formulae, with regard to interpolation. Consequently, each of the four equations tried contain two parameters. The equations, and the results of fitting the data by a least squares method are summarized in Table 7.

Table 7

EQUATIONS TESTED FOR THE PURPOSE OF FITTING THE ISOTHERM DATA

Equation	A	B	r.m.s. deviation of q
$q = Ap/(1 + Bp)$	3.615	.385	.035
$q = A + B \ln p$	2.54	2.26	.07
$q = Ap - Bp^2$	2.66	.293	.13
$q = Ap^B$	2.11	.325	.96

The last of these equations may be rejected immediately, as it neither gives a good fit, nor is it a convenient formula for computation. The second one may also be rejected, on the grounds that it is significantly more difficult to use than either of the remaining two, without giving any improvement in fit. There is very little to choose between the other two; the first one gives a slightly better fit, while the other one will need slightly less computing time if used in the computer programme. However, the fact that the first one is the well known Langmuir[13] isotherm, while the second one has no such association with adsorption theory, led to its choice for use in the computer programme.

The resultant isotherm curve, together with the experimental points is shown in Fig 9 as curve 1. The Linde isotherm is also shown on this plot as curve L. (The origin of curve 2 will be discussed later.)

THE RUNS OF SERIES A

Comparison of Data from Runs 3A and 4A

On the basis of the discussion of Chapter 5, these two runs should produce almost identical breakthrough curves; a glance at the plots reveals that they do not.

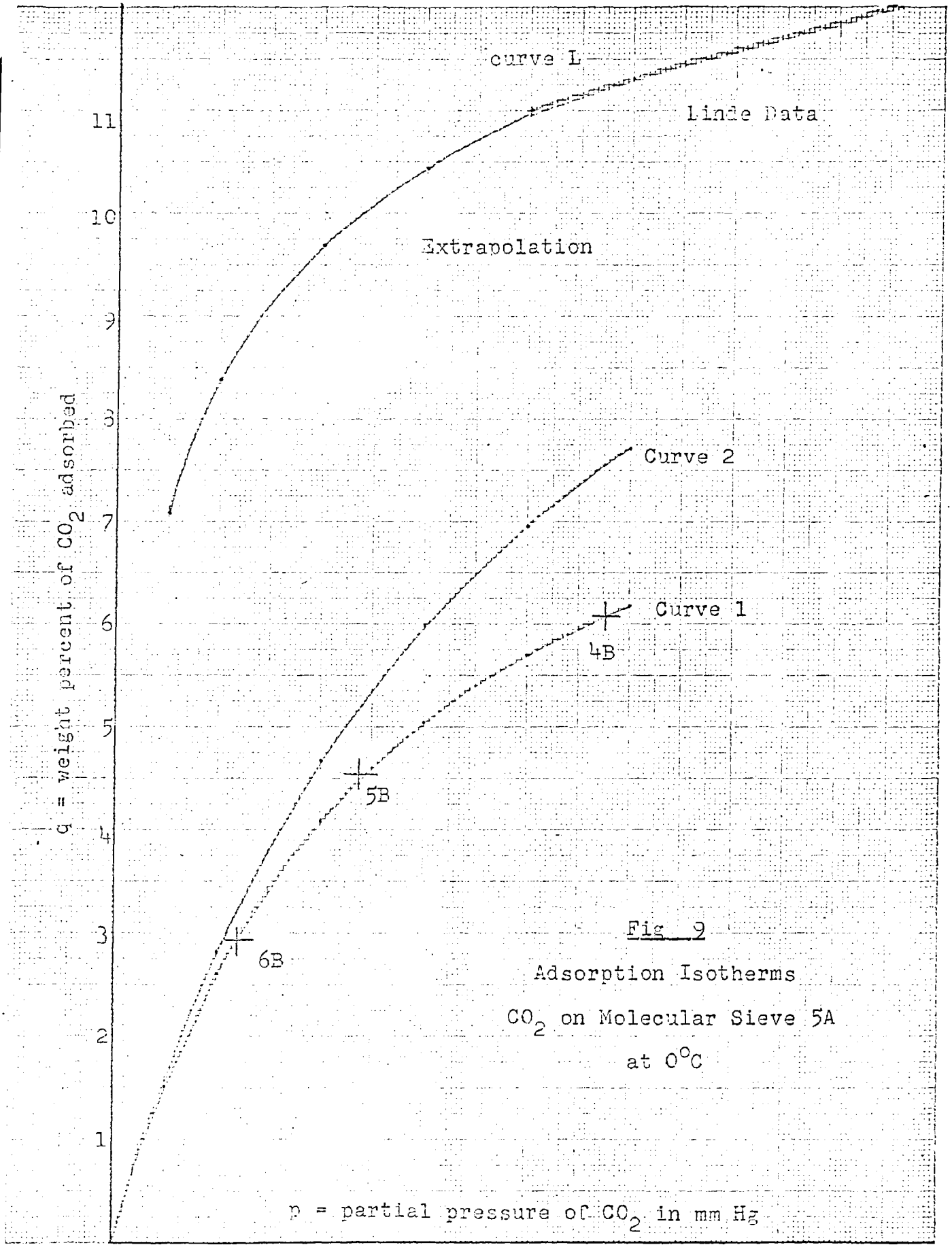


Fig 9

Adsorption Isotherms

CO_2 on Molecular Sieve 5A

at 0°C

The results of the test of reproducibility suggest that the discrepancy is probably not due to experimental error, so one must assume that some physical effect has been overlooked. Two possible explanations come readily to mind: The slightly different shapes of the two sizes of pellet may have resulted in the observed differences, or, it is possible that the two batches of pellets have significantly different "effective isotherms". (Only the isotherm of the 1/16" pellets was measured.) Another, slightly less plausible explanation is that it is not 3A but rather 4A that is "wrong", and that this is so because of the possibility that, at a pressure of 25 ata., either the pellet diffusion coefficient D_p no longer varies inversely with pressure, or the use of partial pressure in the isotherm is no longer valid. Some of these hypotheses can be tested with the help of the computer programme (see chapter 8) but for the present Series A will be treated as two separate groups of runs, with most attention given to Runs 4A, 5A and 6A, for which the isotherm is reasonably well known.

Effect of Variation of the Dimensionless Groups $\frac{S^2}{D_p E}$ and $\frac{S^2}{D_c E}$

Reference to Fig 6 in Chapter 5 shows that a number of groups of points may be selected for the purpose of

determining the separate effects of changes in the two dimensionless groups. The requirement that the points should all belong to Runs 4A, 5A and 6A only (or 1A, 2A and 3A only) limits the choice somewhat, and the fact that not all runs resulted in useful data from all eight points is a further restriction. With these factors in mind, point number two of Run 5A was chosen as the basic one, with the other four points shown in Table 8 providing data at two more levels for each of the dimensionless groups.

Table 8

RELATIVE VALUES OF THE DIMENSIONLESS GROUPS FOR SELECTED POINTS

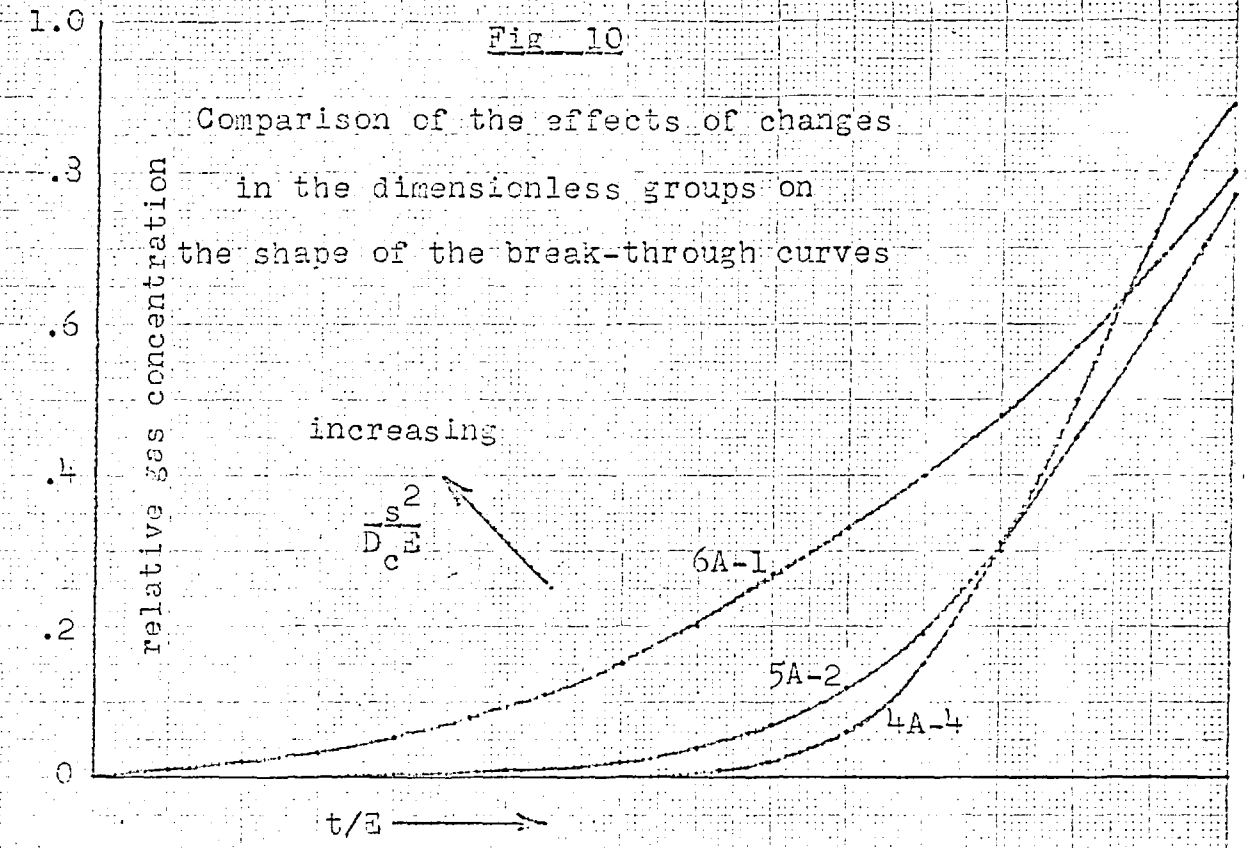
$\frac{D_c E}{s^2}$	$\frac{D_p E}{S^2}$		
	1	2	4
1		6A-1	
2	4A-2	5A-2	6A-2
4		4A-4	

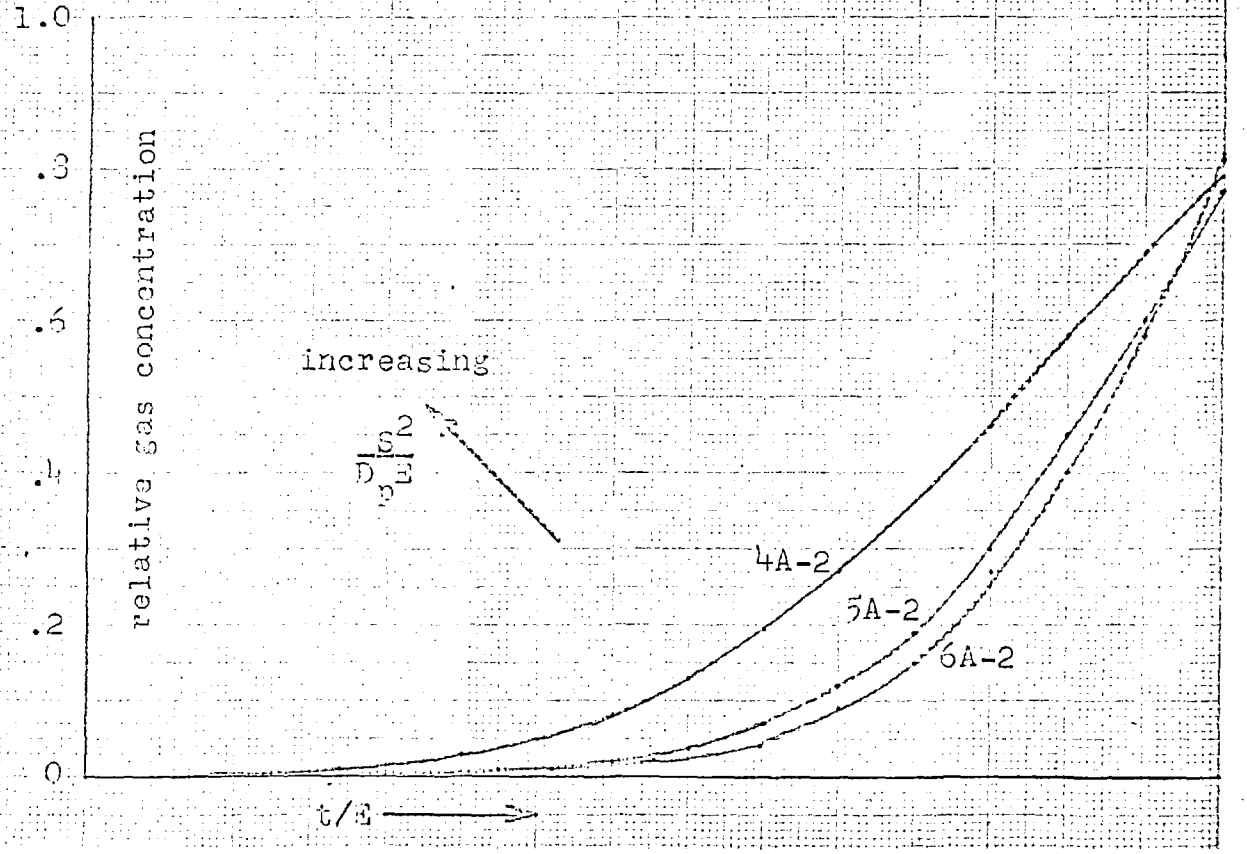
It will be recalled from Chapter 5 that, for the purposes of comparison, breakthrough curves should be plotted against t/E. This has been done for the five points of Table 8, in Figure 10. Examination of this figure reveals that changes in the two dimensionless groups have quite distinctive effects: changes in $\frac{s^2}{D_p E}$ seem to have relatively little influence on the breakthrough time, or on the time at which $C/C_o = .8$, but a considerable effect on the time at which $C/C_o = .4$ Changes in $\frac{s^2}{D_c E}$, on the other hand, do affect breakthrough time. Of course, these qualitative observations are made in a particular neighbourhood of the $\frac{s^2}{D_p E}$ vs $\frac{s^2}{D_c E}$ plane, and their relative importance can be expected to be different in other areas, but it is likely that the nature of the two effects will be preserved. (It is perhaps worth noting here that a similar treatment of data from Runs 1A, 2A and 3A yielded a similar result.)

These important observations may be considered from two points of view: first, because the two effects are essentially different in character, it seems unlikely that an empirical combination of the two diffusion resistances could be used for an effective description of fixed-bed adsorption dynamics. Second, just because

Fig 10

Comparison of the effects of changes in the dimensionless groups on the shape of the break-through curves





the effects are so different, it should be fairly easy to adjust the corresponding parameters in the computer programme developed in Chapter 4, in order to fit the experimental data. This process of data-fitting will be discussed in detail in the next Chapter.

Chapter 8

COMPARISON OF COMPUTED AND EXPERIMENTAL RESULTS

If the values of the physical quantities, such as pellet radius, bed residence time, etc. are used to calculate the parameters X_F, Y_F and E as defined in Chapter 4, the computed break-through curves do not, in general, correspond to the experimental ones. This is not surprising, for two reasons: firstly, the values of some of the quantities (especially those associated with the crystal) are not accurately known, and secondly, the very simple assumptions about tortuosity, void fractions, etc. can be expected to cause errors if no adjustments are made. In the face of these difficulties, two alternatives are available: one may undertake ancillary experiments for the purpose of accurate determination of the required data, and make the requisite adjustments to the theory, or, as was done in this case, one may rely on adjustment of the programme parameters in an empirical fashion in order to fit the experimental data for a given set of conditions. Since it is fairly clear how the parameters will vary with changes in the operating conditions, it should be possible to predict

the values of the parameters over a wide range of conditions, once the values are known for one set of conditions. (This approach is similar to the method adopted for the determination of the isotherm, where the use of an ancillary experiment was rejected in favour of a more complete analysis of fixed bed behaviour.)

METHOD USED TO FIT COMPUTED RESULTS TO EXPERIMENTAL ONES

The basis of the method was mentioned at the end of Chapter 7. Since variation of each of the programme parameters has a different effect, it is possible to adjust them in turn in order to obtain a gradual improvement in fit. Once the shape of the isotherm is established, and the shape factor, α, of the pellets is calculated, only three parameters remain to be determined: E, the bed residence time parameter, X_F, the pellet diffusion parameter, and Y_F, the crystal diffusion parameter. Of these three, E is the easiest to adjust, for two reasons. First, the effect of a change in E is quite different to that of a change in X or Y, and second, because breakthrough curves are obtained for a number of values of E both experimentally

and from the computer runs, data is at hand to allow one to make a well informed guess about the size as well as the sense of the change required. For these reasons, it is advantageous to adjust E first, before changing X or Y. Although the effect of an increase in X is similar to that of an increase in Y, the distinguishing features noted in Chapter 7 are sufficient to enable one to make the correct adjustments. In practice, it was found to be desirable to adjust X before Y, but this need not be used as a rigid rule.

Fitting of Runs 6A, 5A and 4A

This method was used to fit the data of Run 6A. The final choice of parameters, and a plot of the computed curves are presented as Run 6C in Appendix F. Once the data of 6A was fitted, the obvious next step was to use approximately increased values of X to try to fit 5A and 4A, using unchanged values of E and Y. The results of these computer runs are shown in plots 5C and 4C, which may be compared with 5A and 4A respectively.

Fitting of Runs 3A, 2A and 1A

Because the computed results seem to fit the data

of Runs 6A, 5A and 4A quite well, one may conclude that the discrepancy between 4A and 3A is not due to the relatively high pressure used for 4A. Furthermore, the result of variation of α in the programme suggests that this effect is insufficient to explain the differences. So, one must conclude that the effective isotherms of Runs 3A and 4A are significantly different.

Owing to the relatively large value of $\frac{s^2}{D_p}$, it is not possible to make an accurate measurement of the velocity of the adsorption wave front for Run 3A. One can, however, make a rough estimate, which seems to be about 20% less than that for Run 4A. This discrepancy lends further weight to the hypothesis of a different effective isotherm.

In order to determine the shape of this isotherm, another set of three runs, analogous to 4B, 5B and 6B could have been performed for the 1/8" pellets. A different method of determining the isotherm was tried, however, which was surprisingly successful, and did not require further experimentation.

The data of 3A was fitted with the computer programme, using the same parameters as for 4C (but with $\alpha = 1.83$), by variation of the isotherm parameters A

and B. In view of this very circuitous approach, the fit obtained, as shown by comparison of Runs 3A and 3C, is quite remarkable. Furthermore, the fit of Runs 2C and 1C to 2A and 1A respectively is no less good. (The isotherm used is shown as curve 2 in Fig 9.)

THE SIGNIFICANCE OF CHANGES TO THE ISOTHERM

The outcome of this last section may be seen from two points of view. On the one hand, the fit of experimental results by the computed curves could hardly have been better, and the model therefore seems quite acceptable for use in the neighbourhood of the operating conditions studied. But on the other hand, the significantly different isotherm observed for two batches of molecular sieve 5A raises the question of whether or not this sophisticated model is of any real value in such circumstances. For it would be pointless to produce an accurate design based upon one isotherm, if the isotherm (and therefore the performance) of the adsorbent actually used were different.

As a means of illustrating the effect of a change in the shape of the isotherm, Runs 7C and 8C were done with all parameters identical to 4C, but with the isotherm curvature parameter, B, equal to one half of B for Run 4C and B = 0, respectively. (The values of A

were adjusted to make the equilibrium capacity of the adsorber corresponding to the inlet concentration.) If the time at which point number 8 first exceeds .5% is used as a means of comparison, Run 7C will be seen to have a breakthrough time 20% less than Run 4C, and 8C 40% less than 7C.

THE PHYSICAL SIGNIFICANCE OF E, X_F AND Y_F

A set of values for these three parameters was empirically determined and used in Run 6C to fit the data of Run 6A. It was mentioned earlier that it is possible to calculate values of E, X_F and Y_F directly from physical data. This has been done in Appendix G using the operating conditions of Run 6A. The two sets of values are summarized in the table below.

	Obtained by curve fitting	Calculated from physical data
E	27.7 sec *	26.9 sec
X_F	3.6 sec	2.25 sec
Y_F	350 sec	7.14 sec

* see Appendix G

The agreement between the values of E is very good, but this is not really surprising, considering the

method used to obtain the effective isotherm. In fact, if one makes a detailed examination of the assumptions from which the isotherm was determined (and the isotherm parameters computed) one finds that there is probably only one significant source of error: the measurement of flow rates. All other factors are either quite accurately known or else they cancel out when the various calculations are compared. Even flow rate cancels to the extent that it appears in both methods of determining E: the error must therefore arise from a non-linear relationship between actual flow and measured flow.

The agreement between the two values of X_F is not nearly as good as for E, but there are a number of possible explanations for the discrepancy..

1. The difference is equivalent to a tortuosity factor of .465, in comparison to .745 assumed from Dworjanyn's[5E] work. Two factors likely to cause this change are: (a) a wider range of crystal sizes for type 5A than for type 4A. (b) The presence of binder in the pellets used in the present work. (Dworjanyn[5D] used a cylinder packed with pure crystals.)

2. Dworjanyn's[5H] values of V_o and V_2 (the pore-void fraction) were used in the factor $\frac{1-V_o-V_2}{V_2}$ in the

calculation of X_F. The whole of the deviation can be explained by a decrease of 28% in the value of V_2 from .234 to .168 This type of decrease could also result from the presence of binder or from a wider range of crystal sizes. It is therefore quite reasonable that one or both of these factors has caused both an increase in tortuosity and a decrease in pore-void fraction.

3. Because the pellets used were not spheres, it was necessary to use a value of α not equal to two. This introduces the possibility that the diameter of the cylindrical pellets (1/16" in this case) is not the same as the "effective diameter". But the latter would have to exceed the former by over 26% if this were to be the sole explanation of the observed difference, and this does not seem to be likely.

The values of Y_F differ by a factor of about 50. The only sort of "explanation" for this is the observation that in both cases the values were obtained by fitting measured breakthrough curves to computed curves by the variation of a parameter which had a relatively minor effect. Further work is obviously needed to resolve this discrepancy. And in spite of the difficulties with the particular method used by Dworjanyn, it is felt that

experiments on this scale are better suited to measurements of this nature than is the present apparatus.

Chapter 9

CONCLUSIONS

The comparison of computed and experimental results in the previous chapter leads one to the acceptance of the validity of the mathematical model as a means of predicting the dynamic behaviour of a fixed-bed adsorber. Once this conclusion has been drawn, however, it becomes convenient to discuss the results in detail under the familiar headings of Theoretical and Experimental.

THEORETICAL

The Model

A mathematical model of a fixed-bed adsorber has been presented, together with a system of computation which allows solutions to be obtained for a variety of operating conditions. Two new features of this model which contribute to its ability to predict experimental results are the use of a non-linear isotherm, and the inclusion of the effect of diffusion in the sorbed phase. Two effects which have been neglected (apparently justifiably) are diffusional resistance in the fluid film surrounding a pellet, and longitudinal dispersion in the

adsorber. The neglect of these effects has made it possible to use the residence time of the gas in the adsorber as a single parameter to describe both gas flow rate and bed length. This residence time and the diffusion time constants for a pellet and a crystal have been combined in dimensionless groups which simplify the description of the operating conditions.

These three times, and various dimensionless groups formed from them, may be useful apart from their use in the computing system, for example in the comparison of existing experimental data. They may also be used in attempts to devise a more empirical system for adsorber design, for it may well be that the present model is unnecessarily complex. For example, perhaps the effect of crystal diffusion could be incorporated in some less realistic but more easily computed form.

The Computing System

The computing system is undoubtedly capable of improvement: although an attempt was made to make it reasonably efficient, it represents only one combination of the variety of finite difference techniques which are available. Various approaches which were considered in detail but never conclusively tested will be mentioned

to indicate possible areas for future development.

1. An implicit method was used in the present system to integrate the crystal equation. It may be possible to use an explicit method, and thus eliminate the need for solving a set of simultaneous equations for each crystal.

2. In the present system, a set of values of the C_i's guessed and the values of the g_i's are computed from these. It is of course possible to reverse the procedure, and use a set of guessed values of the g_i's to compute the C_i's. The present method was chosen in the hope that it would be less liable to instability, but since the alternative has not been properly tested, no real comparison can yet be made.

3. If crystal diffusion resistance is neglected, a considerable simplification of the computing system is possible. It may be worthwhile to use this simplified model for the first few iterations after each time step, to obtain a good set of values of the C_i's with a minimum of computation. The complete model would then be used for further iterations.

4. Linearization of the isotherm leads to further simplification of the calculations, so this device

may also be useful if employed in the manner described above for crystal diffusion resistance. Either of these methods may prove to be helpful in certain cases, but unnecessary in others. A comprehensive programme of computing experiments may therefore be required in order to find a criterion that would enable one to choose the appropriate technique in a particular case.

In some instances it has been possible to test a variety of techniques before making a choice. Examples are the expressions to evaluate $\frac{\partial C}{\partial l'}$, and the various methods tried for making the next guess of C_i. Although in these cases the "best" of the methods tested were eventually used, there is no way to be sure that a better method did not remain untested. (In the case of a method for guessing C_i, in particular, it is unlikely that further efforts would go unrewarded.)

A different type of improvement is illustrated by the use of an approximate expression for $\nabla^2 C$ near the centre of the pellet. This, which may be described as an approximation to a finite difference approximation, permitted a saving of about 10% in computing time and space: it may be only one of several which could be successfully used.

A shortcoming of the present system, for which it is difficult to prescribe a definite cure, is its instability for extreme values of X_F and Y_F. For the runs of series C, it was possible to overcome this problem by a suitable selection of the finite difference parameters. But since the values of X_F and Y_F may not always lie within the region of stability, it is worthwhile to investigate this problem further. It may be possible to eliminate its cause, but it is more likely that a number of rules will be devised to allow the difficulty to be circumvented. (It may be noted that this type of difficulty is not uncommon in the use of finite difference methods.)

EXPERIMENTAL

With the important exception of the previously noted discrepancy between the experiments on the 1/16" and 1/8" pellets, the experimental results seem to be satisfactorily self-consistent, as well as compatible with the computed results.

The experimental technique embodied no particularly notable innovations, although the range of the apparatus (up to 200 ata and down to -80°C) may be regarded as a significant extension of earlier equipment. (But it

will be noted that this versatility was not fully utilized in the work reported here.)

With the possible exception of the CO_2 analyser, the measuring devices seem to have performed quite accurately. For some of the runs (notably 1A and 2A) the scatter of the analyser output would have been quite intolerable, were it not possible to obtain a sufficiently frequent analysis of each sample point to render an acceptable picture of the true concentration history.

The Data Logging System, although operating far below its capacity, was a valuable aid in the collection of data throughout the lengthy runs that were performed. Its advantages over a human counterpart are threefold: (a) it is less liable to err. (b) It operates continuously over long periods of time. (c) It avoids the necessity of preparing the data for computer analysis.

CONCLUSIONS

The primary aim of this work was to devise a mathematical model which would describe the dynamic behaviour of a fixed-bed adsorber. This appears to have been accomplished fairly successfully. A secondary aim was to use the model to suggest a practical method for the design of industrial adsorbers, Some further questions

will have to be resolved before this can be achieved.

Because the shape of the isotherm is so vital to the performace of the adsorber, some means of ensuring uniformity must be developed. This may be relatively easy for systems other than the one used in this work, and even for the air-CO_2-(water!)-molecular sieve system, the use of a completely standardized routine (not merely for reactivation, but throughout the life of the adsorbent) may result in adequate uniformity.

The present computing system uses more computing time than could probably be justified in the design of all but the largest of adsorbers. It is therefore necessary either to simplify the computer programme significantly, or else to produce a set of charts or tables that could be referred to for the design of any particular adsorber.

Using the present model as an example, four groups of parameters, such as A, BF', $\frac{X_F}{Y_F}$ and $\frac{Y_F}{E}$, would have to be varied to produce tables giving the ratio of the break-through-time t_B, to the residence time, E. In the general case, such tables would have to be hopelessly large to encompass a reasonable variation of each parameter. But if some of the physical variables are fixed (temperature, feed composition and pellet size, for

example) some of the parameters can be restricted as well (A, Y_F and $\frac{BF'Y_F}{X_F}$ in the example). This would enable one to produce a table of $\frac{t_B}{E}$ as a function of E and pressure from a reasonable number of computer runs.

SOME SUGGESTIONS FOR FURTHER WORK

Items of interest suggested by the results of the present work are listed below.

Experimental

1. An investigation of the causes of and cures for the changes in the effective isotherm for CO_2 on molecular sieves, (with particular attention to the effects of water adsorption.)
2. A precise evaluation of D_p and $\frac{s^2}{D_c}$, and an investigation of the effect of changes in operating conditions upon D_p and D_c.
3. A series of fixed-bed adsorber experiments to test the findings of 1. and 2.
4. Another set of fixed-bed experiments to find the limiting pressure for the use of the ideal mixture laws.

Theoretical

1. An investigation of the feasibility of simplifying the model.

2. The improvement of the efficiency of the computing system.

Other items which are of practical interest:

1. The effect of heat of adsorption, encountered for higher concentrations.

2. Multicomponent adsorption, and in particular the Air-CO_2-H_2O-molecular sieve system.

Appendix A

DIFFUSION RESISTANCE IN THE FLUID FILM SURROUNDING THE PELLETS

Chandrasekharan[2B] has shown that this resistance may be neglected for the system that he studied. By comparison of the mass transfer coefficients for his work and for the present work it will be shown that this resistance is even smaller in the present work.

Treybal[14], in his fig 3. 11, gives mass transfer correlations for a number of situations, including the flow of gasses through packed solids. A rough approximation to his curve may be written as follows:

$$\log\left(\frac{.71\ k_y}{G_m}\right) = -.74 - .5 \log\left(\frac{d_p\ U_{av}\ \rho}{\mu}\right)$$, (using Treybal's notation).

For an ideal gas, one may write: $G_m = \frac{273\ P}{22{,}400\ T}\ U_{av}$

$$\rho = \frac{273\ P}{T}\rho_o$$

$$\mu = \frac{T}{273}\mu_o$$

And since both Chandrasekharan's flow rates and those in the present work are based upon Ledoux's Criterion[15]

it is a useful basis for comparison. Using Treybal's notation again, it may be written:

$$(U_{av})^2_{max} = \frac{.0167\, g_c \rho_p d_p}{\rho}$$

After substitution, the mass transfer correlation may be written:

$$\log\left(\frac{k_y T^{.5}}{d_p^{.5} P^{.5}}\right) = \log A - .5 \log\left(\frac{d_p^{1.5} P^{.5}}{T}\right)$$

or $k_y = A\left(\frac{P}{d_p}\right)^{.25}$, where A is a constant which need not be evaluated here.

Because of the higher pressures used in the present work, $\frac{P}{d_p}$ will always exceed the corresponding expression for Chandrasekharan's work, and so the fluid film resistance will be even less.

Appendix B

THE EVALUATION OF α

The surface area of a cylinder of length 1 and radius S is $2\pi S1 + 2\pi S^2$. Its volume is $\pi S^2 1$, so its area/volume ratio is $\left(\frac{2}{S} + \frac{2}{1}\right)$, which compares with the value $\frac{3}{S}$ for a sphere. If one now defines 1_s as being that cylinder length for which the area/volume ratio is that of a sphere, 1_s may be seen to be equal to 2S.

One knows that $\alpha \rightarrow 1$ as $1 \rightarrow \infty$. It seems reasonable to assume that $\alpha \simeq 2$ for $1 = 2S$. It also seems reasonable to use $\alpha = 1 + \frac{2S}{1}$ to interpolate between these two points.

Using this formula, one sees that:

for the $\frac{1}{3}$" pellets $s = \frac{1}{16}$", $1 = \frac{5}{16}$", so $\alpha = 1.83$

and for the $\frac{1}{16}$" pellets $s = \frac{1}{32}$", $1 = \frac{1}{4}$", so $\alpha = 1.55$

One may also note that the area/volume ratio may now be expressed as $\left(\frac{\alpha + 1}{S}\right)$.

Appendix C

COMPUTER PROGRAMMES

The programmes contained in this appendix were originally written in Mercury autocode . They have since been modified in a number of details, and are presently suitable for use with the EXCHLF compiler of the Atlas computer of the Institute of Computer Science. (They can alsc use the less efficient EMA compiler.)

Programme 11 (pages 130 to 138) incorporates the computing system derived in Chapter 4, and was used to produce the plots of series C (given in Appendix F.)

Programme 40/45 (pages 139 to 147) was used to process the experimental data tape in order to produce the plots and tables for runs A and B (given in Appendix F).

Programme 50 (pages 148 to 151) also used the experimental data tape but produced plots of the temperature history of the adsorber, as well as an overall mean temperature for any one run.

Of these three, only the programme 11 requires explanatory notes.

Routine 1 embodies most of the programme, with routines 3 to 6 acting as subroutines to perform

various special functions.

Routine 3 is used to prepare for the use of any particular form of isotherm.

Routine 4 contains the isotherm itself, as well as the procedure used to make the next guess of the Ci's. These two routines have been separated from Routine 1 to facilitate changes in the form of the isotherm.

Routine 5 produces a plot of the breakthrough curves, the only form of output obtained at present. If some other form of output were desired, such as a single number denoting breakthrough time for example, it would be easily obtained by the use of a different "Routine 5".

Routine 6 is also concerned with output format: it produces a heading which describes the set of parameters used.

A method has been devised which allows several runs to be done in succession, each one using its own set of parameters. This permits significant savings in both input and compiling times. Each run may be terminated by any one of three occurrences: (a) If a certain number of time-steps is completed. (b) If the concentration at the outlet to the adsorber exceeds .99 (c) If evidence of

instability is detected during output. The number of iterations for any one time-step has been limited, so that even if the sum of the squares of the deviations of the Ci's still exceeds the specified value after 20 iterations, a new time-step is taken anyway.

```
COMPILER EXCHLF
KWILSON PROGRAMME 11
MAIN-> 2400
AUXILIARY(0,2600)
DEPTH 0
DUMPS 0

ROUTINE 1

S')=4)
4)1005,0,0,5.1
READ(A)
READ(B)
READ(D)
READ(E)
READ(E')
READ(F)
READ(F')
READ(X)
READ(Y)
READ(;)
READ(Q)
READ(R)
READ(S)
READ(T)
READ(R')
READ(Q')

JUMPDOWN(R6)

T'=0
P'=Q'
N=QR
K=RR
L=SS
U=L
V=N
W=S
A'=-E'
G'=0
H'=G'+N
U'=H'+N
V'=U'+N
C'=V'+N
F1=C'+L
I=2(1)N
FI=F1+IS-S
REPEAT
```

```
V1=FN+S
I=2(1)N
VI=V1+IS-S
REPEAT
E1=VN+S
I=2(1)N
EI=E1+I-1
REPEAT
DO=EN+1
D=.000025NDD
Z=ØDIVIDE(SKY+KY,LX)
Y=ØDIVIDE(Y,LT)
X=ØDIVIDE(-3RQX-1.5QX;,KE+KE;)
JUMPDOWN(R3)
B=2/3+2;/3
I=3(1)L
CI=0
REPEAT
C1=-1
C2=+1
C(L-1)=1
CL=-1
P=S-1
J=2(1)P
I=JS+J-S
C(I-1)=.5-.5/J
CI=-1
C(I+1)=1-C(I-1)
REPEAT
Ø7(G')C1,L
U'=Ø20(G',Y,W)
C'=Ø19(G',Y,W)
G'=Ø15(U',U)
C'=Ø28(U',S,S)
C'=Ø14(C',2,C',L)
V'=Ø29(1,W)
V'=Ø28(G',S,S)
I=1(1)S
D'=V'+IS-1
Ø6(D')DI,1
DI=ZDI
REPEAT
```

```
Ø7(DO)D1,S
CO=1
I=1(1)N
AI=0
BI=0
CI=0
GI=0
UI=0
XI=0
YI=0
ZI=0
REPEAT
J=2S
I=0(1)J
Ø7(F1+IN)A1,N
REPEAT
Ø7(H')A1,N
1)J'=2R
H1=-1.25+CR+.25CJ'
I'=N
J'=N-R
K'=N-2R
L'=N-3R
HQ=1.5CI'-2CJ'+.5CK'
H(Q-1)=CI'/3+.5CJ'-CK'+CL'/6
P=Q-2
I=2(1)P
I'=IR-2R
J'=I'+R
K'=J'+2R
L'=K'+R
HI=CI'/12-2CJ'/3+2CK'/3-CL'/12
REPEAT
I=1(1)Q
J'=IR
I'=J'-R
JUMP 2,0≥HI
K'=J'+R
HI=.5CK'-.5CI'
2)GJ'=2C(J'-1)-2CJ'+XHI
G(I'+1)=-BC(I'+1)+BC(I'+2)
P=R-1
J=2(1)P
K'=J'-R+J
Z'=.5;/J
Y'=1-Z'
Z'=1+Z'
GK'=Y'C(K'-1)-2CK'+Z'C(K'+1)
REPEAT
REPEAT
```

```
I=1(1)N
JUMP 3,GI>0
ø6(H'+I-1)GI,1
3)REPEAT
ø7(G')G1,N
U'=ø11(G',H',V)
V'=ø13(E1,DS,U',V)
ø6(V')B1,N

JUMPDOWN(R4)

C=C+1
JUMP 9,D>C
JUMP 1,20>C
9)T'=T'+1
P'=P'-1
JUMP 10,P'>0
P'=Q'

JUMPDOWN(R5)

10)C=0
ø6(H')B1,N
I=1(1)N
BI=BI+GI
VI=ø13(FI,BI,DO,W)
FI=ø20(C',VI,W,1,V)
D'=FI+S-1
EI=ø15(D',1)
UI=CI
AI=0
XI=0
YI=0
ZI=0
REPEAT
ø7(H')G1,N
JUMP 4,T'>R'
JUMP 1,.99>CN
JUMP 4

RETURN
**

ROUTINE 3

A=6035.6A
B'=BF'

RETURN
**
```

```
ROUTINE 4

C=0
I=1(1)N
BI=ØDIVIDE(-BI,A+B'BI)
JUMP 5,BI>UI
BI=UI
5)JUMP 6,1>BI
BI=1
6)JUMP 2,BI=CI
JUMP 7,C>D
WI=ØDIVIDE(BI-CI,BI+CI)
C=C+WIWI
7)JUMP 9,BI>CI
JUMP 26,AI=ZI
JUMP 26,ZI>CI
WI=ØDIVIDE(XI-BI,BI-CI)
JUMP 3,WI>E'
JUMP 3,A'>WI
26)XI=BI
YI=CI
CI=FBI+CI-FCI
JUMP 2
3)XI=BI
YI=CI
JUMP 13
9)JUMP 25,XI=YI
JUMP 25,CI>YI
WI=ØDIVIDE(AI-BI,BI-CI)
JUMP 4,WI>E'
JUMP 4,A'>WI
25)AI=BI
ZI=CI
CI=FBI+CI-FCI
JUMP 2
4)AI=BI
ZI=CI
13)CI=ØDIVIDE(AIYI-XIZI,AI+YI-XI-ZI)
2)REPEAT
RETURN
**
```

```
ROUTINE 5

Z'=ØFRPT(.2T'/Q'+.0000005)
JUMP 111,.000001>Z'
I=1(1)7
SPACE
REPEAT
115)PUNCH(3)
K'=Q
J'=N
I=Q(-1)1
Z'=ØFRPT(I/10+.03)
I'=ØINTPT(10Z')
I'=ØTABLE(116,I')
L'=K'
K'=ØINTPT(100CJ'+.5)
JUMP 112,K'=L'
O'=K'-L'-2
JUMP 113,O'=-1
JUMP 118,O'>-1
UP LEVEL
JUMP (S')
118)J=O(1)O'
SPACE
REPEAT
113)PUNCH(I')
112)J'=J'-R
REPEAT
K'=99-K'
JUMP 114,K'=-1
JUMP 117,K'=0
I=1(1)K'
SPACE
REPEAT
117)PUNCH(3)
JUMP 114
111)PRINT(.1T'/Q')2,1
JUMP 115
116)INTEGERS 16,1,2,10,4,21,22,7,8,25,16
114)NEWLINE

RETURN
**
```

```
ROUTINE 6

READ(J)
NEWLINE
JUMPDOWN 1
CAPTION
PLOT OF COMPUTED BREAKTHROUGH CURVES
NEWLINE
NEWLINE
JUMPDOWN 1
CAPTION
     COMPUTER RUN NUMBER
PRINT(J)2,0
CAPTION
C
NEWLINE
NEWLINE
NEWLINE
JUMPDOWN 2
CAPTION
      PROGRAMME PARAMETERS
JUMPDOWN 3
CAPTION
FINITE-DIFFERENCE PARAMETERS
NEWLINE
NEWLINE
JUMPDOWN 2
CAPTION
BED  RESIDENCE  TIME    (E)=
PRINT(E)3,2
JUMPDOWN 3
CAPTION
NUMBER OF STEPS IN BED  LENGTH    (Q)=
PRINT(Q)2,0
NEWLINE
JUMPDOWN 2
CAPTION
PELLET  RESISTANCE      (X)=
PRINT(X)3,2
```

```
JUMPDOWN 3
CAPTION
NUMBER OF STEPS IN PELLET RADIUS (R)=
PRINT(R)2,0
NEWLINE
JUMPDOWN 2
CAPTION
CRYSTAL  RESISTANCE     (Y)=
PRINT(Y)3,2
JUMPDOWN 3
CAPTION
NUMBER OF STEPS IN CRYSTAL RADIUS(S)=
PRINT(S)2,0
NEWLINE
JUMPDOWN 2
CAPTION
PELLET SHAPE FACTOR (ALPHA)=
PRINT(;)2,2
JUMPDOWN 3
CAPTION
NUMBER OF MINUTES IN TIME-STEP  (T)=
PRINT(6/Q')1,1
I=1(1)5
NEWLINE
REPEAT
CAPTION
HOURS
JUMPDOWN 1
CAPTION
GAS CONCENTRATION
NEWLINE
JUMP 4
1)I=1(1)36
SPACE
REPEAT
RETURN
2)I=1(1)13
SPACE
REPEAT
RETURN
3)I=1(1)8
SPACE
REPEAT
RETURN

4)RETURN
**
```

```
CHAPTER 0


A->192
B->192
C->192
D->  7
E->192
F->192
G->192
H-> 32
U->192
V->192
W->192
X->192
Y->192
Z->192

CHANNEL 1P
CHANNEL 1R

JUMPDOWN(R1)

CLOSE
***Z
```

```
COMPILER EXCHLF
KWILSON PROGRAMME 40/45
MAIN->50
AUXILIARY(0,0)
DEPTH 0
DUMPS 0

ROUTINE 41

CHANNEL 1R
I=0(1)2
READ(E1)
REPEAT
READ(Y)
READ(U')
READ(F')
READ(G)
READ(H)
READ(V)
READ(D)
READ(T)
READ(S)
CHANNEL 2R

RETURN
**

ROUTINE 42

CHANNEL 1P
U=DV-DG
V=H-G
H=100/U
V=90U/V
NEWLINE
CAPTION
        PLOT OF EXPERIMENTAL BREAKTHROUGH CURVES
NEWLINE
NEWLINE
CAPTION
        EXPERIMENT NUMBER
PRINT(E0)1,0
JUMP 1,E1>1.5
```

```
CAPTION
A
JUMP 2
1)CAPTION
B
2)NEWLINE
NEWLINE
CAPTION
       EXPERIMENTAL CONDITIONS
NEWLINE
NEWLINE
JUMP 3,E2>1.5
CAPTION
       MOLECULAR SIEVE TYPE 5A,1/16 INCH DIAMETER CYLINDERS
JUMP 4
3)CAPTION
       MOLECULAR SIEVE TYPE 5A,1/8 INCH DIAMETER CYLINDERS
4)NEWLINE
CAPTION
       PRESSURE,
PRINT(Y)11,2
CAPTION
ATMOSPHERES ABSOLUTE
NEWLINE
CAPTION
       TEMPERATURE,
PRINT(U')9,1
CAPTION
DEGREES CELSIUS
NEWLINE
CAPTION
       AIR FLOW RATE,
PRINT(F')6,2
CAPTION
STANDARD CUBIC FEET PER MINUTE
NEWLINE
CAPTION
       FEED CONCENTRATION,
PRINT(V)4,0
CAPTION
PARTS PER MILLION OF CO2
NEWLINE

RETURN
**
```

```
ROUTINE 47

CHANNEL 2P
NEWLINE
CAPTION
                TABULATION OF 1000C/C0 AS A FUNCTION OF TIME AND BED LENGTH
NEWLINE
NEWLINE
CAPTION
                EXPERIMENT NUMBER
PRINT(E0)1,0
JUMP 1,E1>1.5
CAPTION
A
JUMP 2
1)CAPTION
B
2)NEWLINE
NEWLINE
CAPTION
                EXPERIMENTAL CONDITIONS
NEWLINE
NEWLINE
JUMP 3,E2>1.5
CAPTION
                MOLECULAR SIEVE TYPE 5A,1/16 INCH DIAMETER CYLINDERS
JUMP 4
3)CAPTION
                MOLECULAR SIEVE TYPE 5A,1/8 INCH DIAMETER CYLINDERS
4)NEWLINE
CAPTION
                PRESSURE,
PRINT(Y)11,2
CAPTION
ATMOSPHERES ABSOLUTE
NEWLINE
CAPTION
                TEMPERATURE,
PRINT(U')9,1
CAPTION
DEGREES CELSIUS
NEWLINE
CAPTION
                AIR FLOW RATE,
PRINT(F')6,2
CAPTION
STANDARD CUBIC FEET PER MINUTE
```

```
NEWLINE
CAPTION
                FEED CONCENTRATION,
PRINT(V)4,0
CAPTION
PARTS PER MILLION OF CO2
NEWLINE
NEWLINE
NEWLINE
CAPTION
SAMPLE POINT NO.   0     1     2     3     4     5     6     7     8
NEWLINE
CAPTION
TIME OF SAMPLE     T     T+1   T+2   T+3   T+4   T+5   T+1   T+2   T+3
NEWLINE
CAPTION
ELAPSED TIME (T)
NEWLINE
CAPTION
IN MINUTES
NEWLINE

RETURN
**

ROUTINE 4

I=1(1)11
READ(Z')
REPEAT
X=Z'-G
JUMP 11,X≥0
X=0
11)READ(P)
READ(J)
Z=ØTABLE(12,J)
X=HXZ
JUMP 14
12)0
1
10
100

14)RETURN
**
```

```
ROUTINE 43

CHANNEL 2P
L=0(1)5
JUMPDOWN(R4)
BL=X
CL=X
DL=P
REPEAT
J=0
JUMP 1,D1=1
J=1
JUMP 1,D2=2
J=2
JUMP 1,D3=3
J=3
JUMP 1,D4=4
J=4
1)I'=7J
J'=1+J
NEWLINE
PRINT(Q)5,0
Q=Q+6
I=1(1)8
SPACE
REPEAT
PRINT(10C0)4,0
JUMP 2,J=0
I=1(1)I'
SPACE
REPEAT
2)I=J'(1)5
PRINT(10C1)4,0
REPEAT
JUMP 3,J=0
I=1(1)J
PRINT(10C1)4,0
REPEAT
3)L=0(1)5
JUMPDOWN(R4)
CL=X
DL=P
REPEAT
```

```
X0=C0
X1=2B1+C1/7
X2=1.25B2+.0625C2
X3=B3
X4=0
X5=0
J=0
JUMP 4,D1=1
J=1
JUMP 4,D2=2
J=2
JUMP 4,D3=3
J=3
JUMP 4,D4=4
J=4
4)I'=7J
J'=1+J
NEWLINE
PRINT(Q)5,0
Q=Q+6
I=1(1)8
SPACE
REPEAT
PRINT(10C0)4,0
JUMP 5,J=0
I=1(1)I'
SPACE
REPEAT
5)I=J'(1)5
PRINT(10CI)4,0
REPEAT
JUMP 6,J=0
I=1(1)J
PRINT(10CI)4,0
REPEAT
6)CHANNEL 1P
NEWLINE
NEWLINE
I=1(1)7
SPACE
REPEAT
PUNCH(3)
RETURN
**
```

```
ROUTINE 45

CHANNEL 2P
I=0(1)5
JUMPDOWN(R4)
AL=BL
BL=CL
CL=X
DL=P
REPEAT
X0=.5B0+.5C0
X1=-A1/9+8B1/9+2C1/9
X2=-A2/13+77B2/78+7C2/78
X3=B3
X4=7A4/78+77B4/78-C4/13
X5=2A5/9+8B5/9-C5/9
J=0
JUMP 1,D1=1
J=1
JUMP 1,D2=2
J=2
JUMP 1,D3=3
J=3
JUMP 1,D4=4
J=4
1)I'=7J
J'=1+J
NEWLINE
PRINT(Q)5,0
Q=Q+6
I=1(1)8
SPACE
REPEAT
PRINT(10C0)4,0
JUMP 2,J=0
I=1(1)I'
SPACE
REPEAT
2)I=J'(1)5
PRINT(10CI)4,0
REPEAT
JUMP 3,J=0
I=1(1)J
PRINT(10CI)4,0
REPEAT

3)RETURN
**
```

```
ROUTINE 56

CHANNEL 1P
L=0(1)5
XL=ØINTPT(XL+.5)
JUMP 8,XL>0
XL=0
8)XL=XL+.1L
REPEAT
I=0(1)4
J=I+1
A=XI
K=J(1)5
B=XK
JUMP 3,B>A
C=A
A=B
XK=C
XI=A
3)REPEAT
REPEAT
NEWLINE
S=S+6T
Z=ØFRPT(S/30)
JUMP 111,Z=0
I=1(1)7
SPACE
REPEAT
115)PUNCH(3)
K'=0
I=0(1)5
L'=K'
K'=ØINTPT(XI)
JUMP 112,K'=L'
O'=K'-L'-2
Y=ØFRPT(XI)
Y=10Y+.5
I'=ØINTPT(Y)
M=ØTABLE(15,I')
JUMP 113,0>O'
J=0(1)O'
SPACE
REPEAT
```

```
113)PUNCH(M)
112)REPEAT
K'=99-K'
JUMP 114,0>K'
JUMP 117,K'=0
I=1(1)K'
SPACE
REPEAT
117)PUNCH(3)
JUMP 114
111)PRINT(S/60)2,1
JUMP 115
15)INTEGERS 16,1,2,19,4,21,22,7,8,25

114)RETURN
**

CHAPTER 0

A->5
B->5
C->5
D->5
E->2
X->5

JUMPDOWN(R41)
JUMPDOWN(R42)
JUMPDOWN(R47)
JUMPDOWN(R43)
JUMPDOWN(R56)
45)JUMPDOWN(R45)
JUMPDOWN(R56)
JUMP 45

CLOSE
***Z
```

```
COMPILER EXCHLF
KWILSON PROGRAMME 50
MAIN->25
AUXILIARY(0,0)
DEPTH 0
DUMPS 0

ROUTINE 51

CHANNEL 1R
READ(D')
READ(A)
READ(B)
READ(Z)
READ(T)
CHANNEL 2R

RETURN
**

ROUTINE 52

C=Z-A
C=C/5.4
W=Z-B
W=W/5.4
D=A-B
F=100/D
C=FA
H'=1000
CAPTION
PLOT OF BED TEMPERATURES,FOR THE RUN OF
PRINT(D')2,2
CAPTION
1965
NEWLINE
NEWLINE
CAPTION
LAW SCALE TEMPERATURE  =
PRINT(C)2,1
CAPTION
DEGREES CENTIGRADE
NEWLINE
CAPTION
FULL SCALE TEMPERATURE =
PRINT(W)2,1
CAPTION
DEGREES CENTIGRADE

RETURN
**
```

```
ROUTINE 4

READ(UO)
JUMP 3,1000>UO
NEWLINE
CAPTION
MEAN OUTPUT FOR FEED CONCENTRATION=
X=S+6T
PRINT(6TO'/X)3,1
NEWLINE
CAPTION
SMALLEST OUTPUT=
PRINT(H')3,0
NEWLINE
CAPTION
MEAN TEMPERATURE=
X=S/T+M+1
C'=Z-.1C'/X
PRINT(C'/5.4)2,1
CAPTION
DEGREES CELSIUS
END
3)C'=C'+UO
L=1(1)9
READ(UL)
C'=C'+UL
REPEAT
READ(E')
READ(F')
JUMP 1,F'>0
G'=G'+E'
1)JUMP 2,E'>H'
H'=E'
2)READ(E')
RETURN
**

ROUTINE 55

L=0(1)9
XL=0
REPEAT
M=0(1)5
JUMPDOWN(R4)
L=0(1)9
XL=XL+UL
REPEAT
REPEAT
```

```
L=0(1)9
XL=G-FXL/6+.5
XL=ØINTPT(XL)
XL=XL+.1L
REPEAT
I=0(1)8
J=I+1
U=XI
K=J(1)9
V=XK
JUMP 3,V>U
W=U
U=V
XK=W
XI=U
3)REPEAT
REPEAT

RETURN
**

ROUTINE 56

NEWLINE
S=S+6T
Z'=ØFRPT(S/30)
JUMP 111,Z'=0
I=1(1)7
SPACE
REPEAT
115)PUNCH(3)
K'=0
I=0(1)9
L'=K'
K'=ØINTPT(XI)
JUMP 112,K'=L'
G'=K'-L'-2
Y=ØFRPT(XI)
Y=10Y+.5
I'=ØINTPT(Y)
M=ØTABLE(15,I')
JUMP 113,0>0'
J=0(1)0'
SPACE
REPEAT
```

```
113)PUNCH(M)
112)REPEAT
K'=99-K'
JUMP 114,K'=-1
JUMP 117,K'=0
I=1(1)K'
SPACE
REPEAT
117)PUNCH(3)
JUMP 114
111)PRINT(S/60)2,1
JUMP 115
15)INTEGERS 16,1,2,19,4,21,22,7,8,25

114)RETURN
**

CHAPTER 0

U->0
X->0

JUMPDOWN(R51)
JUMPDOWN(R52)
55)JUMPDOWN(R55)
JUMPDOWN(R56)
JUMP 55
CLOSE
***Z
```

Appendix D

CALCULATIONS TO AID THE CHOICE OF THE FINITE DIFFERENCE PARAMETERS

D was defined in Chapter 4 as $(\underset{\sim}{A} - Y\underset{\sim}{I})^{-1} \begin{bmatrix} 0 \\ 0 \\ \cdot \\ \cdot \\ 0 \\ 1 \end{bmatrix} Z$

The terms of D may be evaluated fairly easily for small values of s. For example, when s = 3 (and substituting X for 1 + Y)

$$\underset{\sim}{A} = \begin{pmatrix} -1 & 1 & 0 \\ 1/4 & -1 & 3/4 \\ 0 & 1 & -1 \end{pmatrix}, \quad (\underset{\sim}{A} - Y\underset{\sim}{I}) = \begin{pmatrix} -X & 1 & 1 \\ 1/4 & -X & 3/4 \\ 0 & 1 & -X \end{pmatrix}$$

$$(\underset{\sim}{A} - Y\underset{\sim}{I})^{\#} = \begin{pmatrix} X^2 - 3/4 & X/4 & 1/4 \\ X & X^2 & X \\ 3/4 & 3X/4 & X^2 - 1/4 \end{pmatrix}, \quad \left|\underset{\sim}{A} - Y\underset{\sim}{I}\right| = -X^3 - X$$

Accordingly, $D_1 = \dfrac{3/4}{-X^3 + X} Z = -\dfrac{3Z}{8Y} \dfrac{1}{1 + 3Y2 + Y^2/2}$

$$D_2 = \frac{3X/4}{-X^3 + X} Z = -\frac{3Z}{8Y} \frac{1 + Y}{1 + 3Y/2 + Y^2/2}$$

$$D_3 = \frac{X^2 - 1/4}{-X^3 + X} Z = -\frac{3Z}{8Y} \frac{1 + 8Y/3 + 4Y^2 3}{1 + 3Y2 + Y^2/2}$$

If similar calculations are repeated for other values of s, three conclusions can be drawn (if the D_i's are expressed in terms of Y rather than X): (a) the general expression corresponding to the factor $\frac{3}{8}$ is $\frac{3}{2(s+1)}$. (b) The numerator of D_i is a function of i only and is the same for all values of s. (c) The denominator of D_i is a function of s only and is the same for all i.

Considering the numerators first, if they are re-expressed in terms of $\bar{X}$, it becomes possible to discern a number of rules which can be used to generate the expressions for the numerators for all values of i. The following matrix gives the polynomial coefficients of the numerators for values of i from 1 to 8. (The coefficients have been expressed as unreduced fractions to help to illustrate the means by which the rules were obtained.)

	j=1	2	3	4	5	6	7	8
	1	X	X^2	X^3	X^4	X^5	X^6	X^7
i=1	1/1							
2	0	2/2						
3	-1/3	0	4/3					
4	0	-4/4	0	8/4				
5	1/5	0	12/5	0	16/5			
6	0	6/6	0	-32/6	0	32/6		
7	-1/7	0	24/7	0	-80/7	0	64/7	
8	0	-8/8	0	80/8	0	-192/8	0	128/8

Three rules are sufficient to describe the terms of this matrix:

1. Elements above the main diagonal are zero.
2. The elements of the first column are contained in the series: 1/1, 0, -1/3, 0, 1/5, 0, -1/7, 0 ...
3. Subsequent elements along the diagonals are formed by multiplication of the preceding element by $\frac{(i+j-2)(i-1)}{i(j-1)}$ where i is the row number and j is the the column number of the new element.

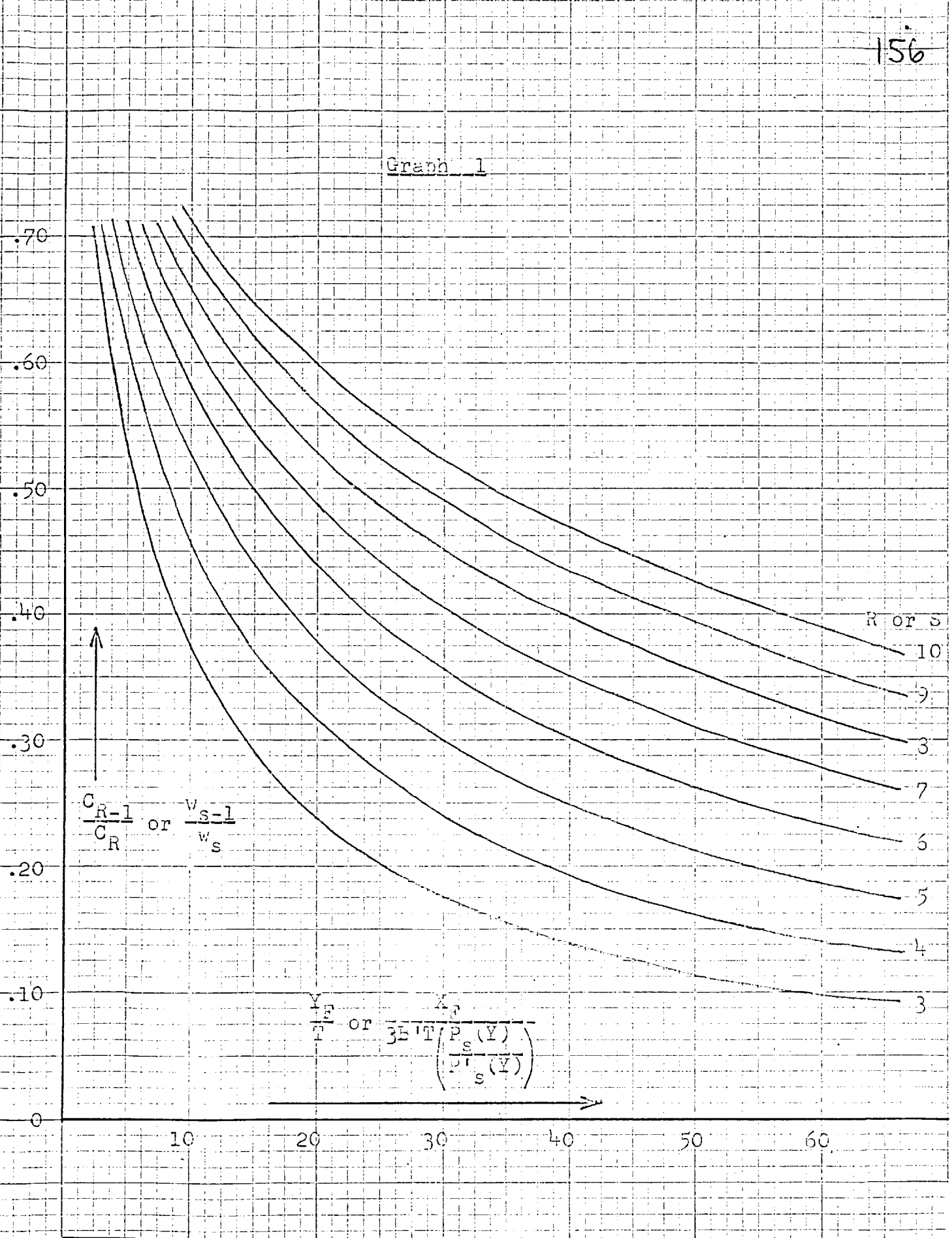
These rules were incorporated into a small computer programme which was used to calculate $\frac{D_{s-1}}{D_s}$ $\left(\text{or } \frac{W_{s-1}}{W_s}\right)$ for s = 3, 4, 5, ... 10 and

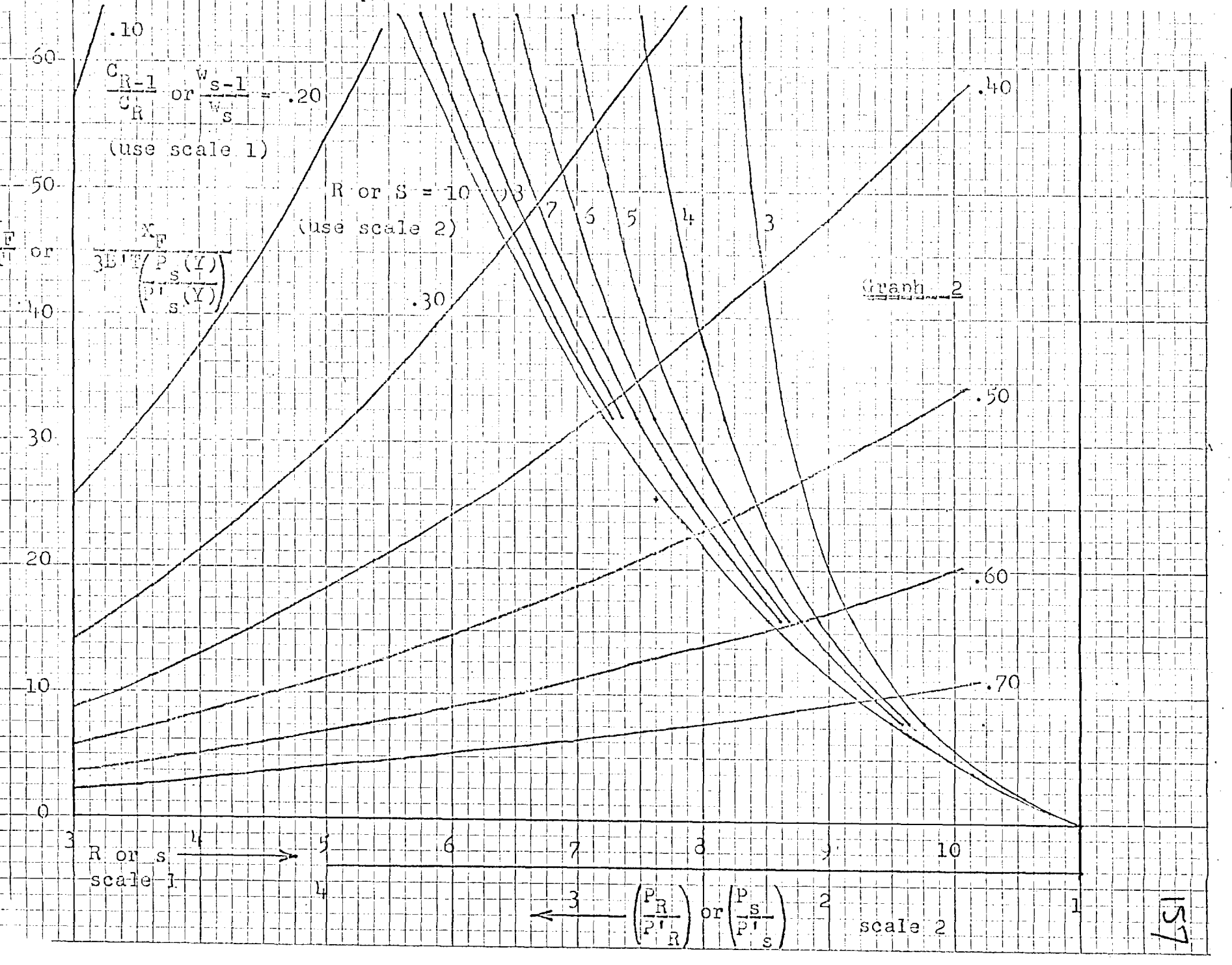
Y = 1, 2, 4, . . . 64. The results of these calculations are plotted in graph 1 in the form of contours of fixed s in the $\frac{w_{s-1}}{w_s}$ - $\frac{Y_F}{T}$ plane. In order to facilitate their use in the manner proposed in Chapter 4, the same results were replotted in the $\frac{Y_F}{T}$ - s plane in graph 2. (As noted in Chapter 4, alternative coordinates for both graphs are $\frac{C_{R-1}}{C_R}$, $\frac{X_F}{3B'T\left(\frac{P_s(Y)}{P'_s(Y)}\right)}$ and R.)

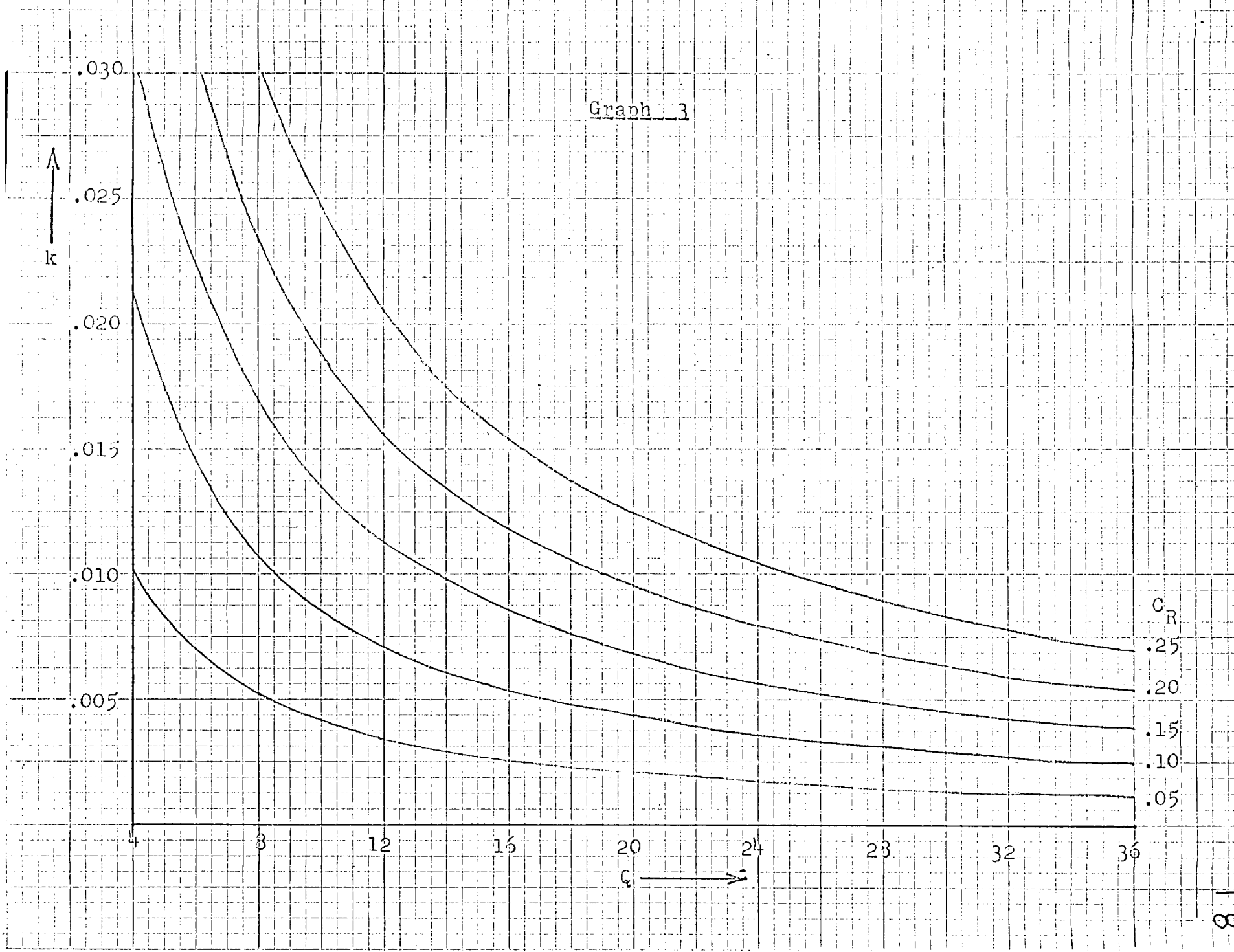
In a similar manner, one may obtain rules for evaluating $\left(\frac{P_s(Y)}{P'_s(Y)}\right)$ for a series of values of s and Y. The calculations were again done on the computer, and the results are also plotted in graph 2.

Graph 3 is merely a display of the function $kQ = \frac{C_R}{\frac{5}{4} - C_R}$, which will be found to be useful in the choice of Q.

Graph 1


.70
.60
.50
.40
.30
.20
.10
0
10
20
30
40
50
60
R or S
10
9
8
7
6
5
4
3
$\frac{C_R - 1}{C_R}$ or $\frac{W_s - 1}{W_s}$
$\frac{Y_F}{T}$ or $\frac{X_F}{3E'T\left(\frac{P_s(Y)}{P'_s(Y)}\right)}$


.10
$\frac{C_{R-1}}{C_R}$ or $\frac{W_{s-1}}{W_s}$ = .20
(use scale 1)
R or S = 10 9 8 7 6 5 4 3
(use scale 2)
$\frac{X_F}{BET\left(\frac{P_s(Y)}{P'_s(Y)}\right)}$
.30
.40
.50
.60
.70
Graph 2
60
50
40
30
20
10
0
3 4 5 6 7 8 9 10
R or s
scale 1
4 3 2 1
$\left(\frac{P_R}{P'_R}\right)$ or $\left(\frac{P_s}{P'_s}\right)$
scale 2


Graph 3
k
.030
.025
.020
.015
.010
.005
C_R
.25
.20
.15
.10
.05
4
8
12
16
20
24
28
32
36
C_L

Appendix E

CHOICE OF FLOW RATES, BASED UPON LEDOUX'S CRITERION

Ledoux's Criterion[15] was used in Appendix A, where it was written in Treybal's notation. It is rewritten below in a more general form:

$$\frac{(\text{mass velocity of gas})^2}{(\text{gas density})(\text{solid density})(\text{solid diameter})} = .0167 \text{ g}$$

Since the only conditions varied in the present series of experiments were pressure, flow rate and pellet size, it is possible to rewrite Ledoux's Criterion in the form of an expression for maximum flow rate as a function of pressure and pellet diameter only - i.e. $(F)_{max} = 23.95 \sqrt{PD}$, where F is in SCFM, P in ata. and D in inches.

In a similar manner, the residence time E may be expressed as a function of P and F. $E = \frac{4.5\ P}{F}$. Combining these two, one obtains an expression for $(E)_{min} = .188\sqrt{\frac{P}{D}}$

Of the six runs of series A, $(E)_{min}$ will have its maximum value of 3.76 sec for Run 4A, where P = 25 ata

and D = 1/16". A value of 7.5 sec, almost double this, was adopted as basic in order to have a margin of safety. (For runs 4B, 5B and 6B, E will be seen to be only half of this basic value. But since the pressure for these runs is only 6.25 ata, the value of $(E)_{min}$ is 1.88 sec and so the previous margin of safety is maintained.)

From the previous expression for E, it will be seen that $F = \frac{4.5P}{7.5} = .6P$ Thus, when P = 25 ata, F = 15 SCFM, and so on.

Appendix F

PRESENTATION OF RESULTS

This appendix contains a set of plots of the experimental and computed breakthrough curves, and a set of tables of the experimental analyses. They were produced by obtaining the output from programmes 11 and 40/45 on punched papertape, which was then read on "flexowriters" to obtain the required number of copies. (This method was used because the standard printed output from the computer is not suitable for binding.)

The plots have been grouped together to facilitate the comparison of various runs. In particular, the experimental runs of series A are interleaved with the corresponding computed runs of series C. If two plots to be compared are unfolded and superimposed, it is then possible to see both sets of curves at once.

PLOTS

Run Number	Page Number
1A	163
1C	164
2A	165
2C	166
3A	167
3C	168
4A	169
4C	170
5A	171
5C	172
6A	173
6C	174
7C	175
8C	176
1B	177
2B	178
3B	179
4B	180
5B	181
6B	182

TABLES

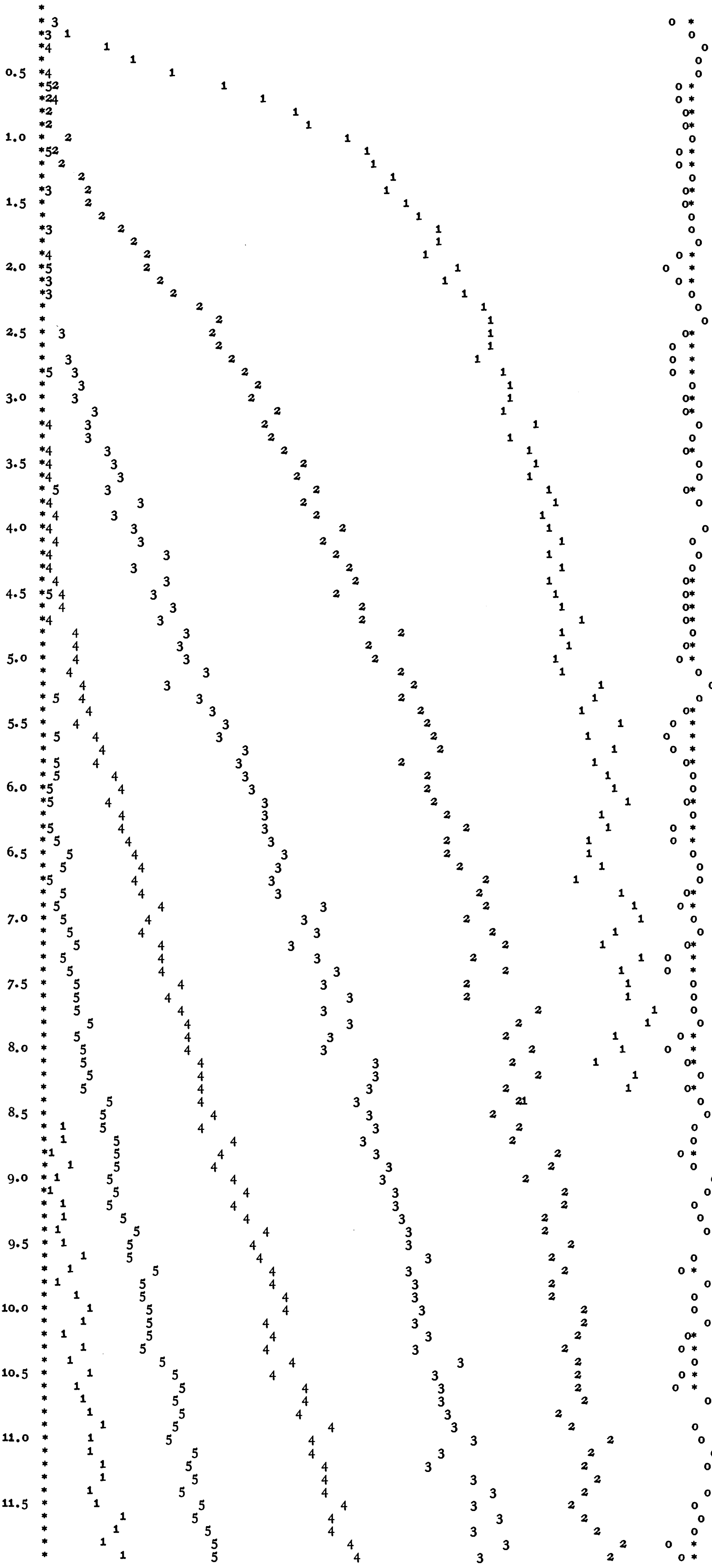
Run Number	Page Number
1A	183
2A	184
3A	185
4A	186
5A	187
6A	188
1B	189
2B	190
3B	191
4B	192
5B	193
6B	194

PLOT OF EXPERIMENTAL BREAKTHROUGH CURVES

EXPERIMENT NUMBER 1 A

EXPERIMENTAL CONDITIONS

MOLECULAR SIEVE TYPE 5A,1/8 INCH DIAMETER CYLINDERS
PRESSURE, 25.00 ATMOSPHERES ABSOLUTE
TEMPERATURE, 1.4 DEGREES CELSIUS
AIR FLOW RATE, 15.00 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 249 PARTS PER MILLION OF CO2



PLOT OF COMPUTED BREAKTHROUGH CURVES

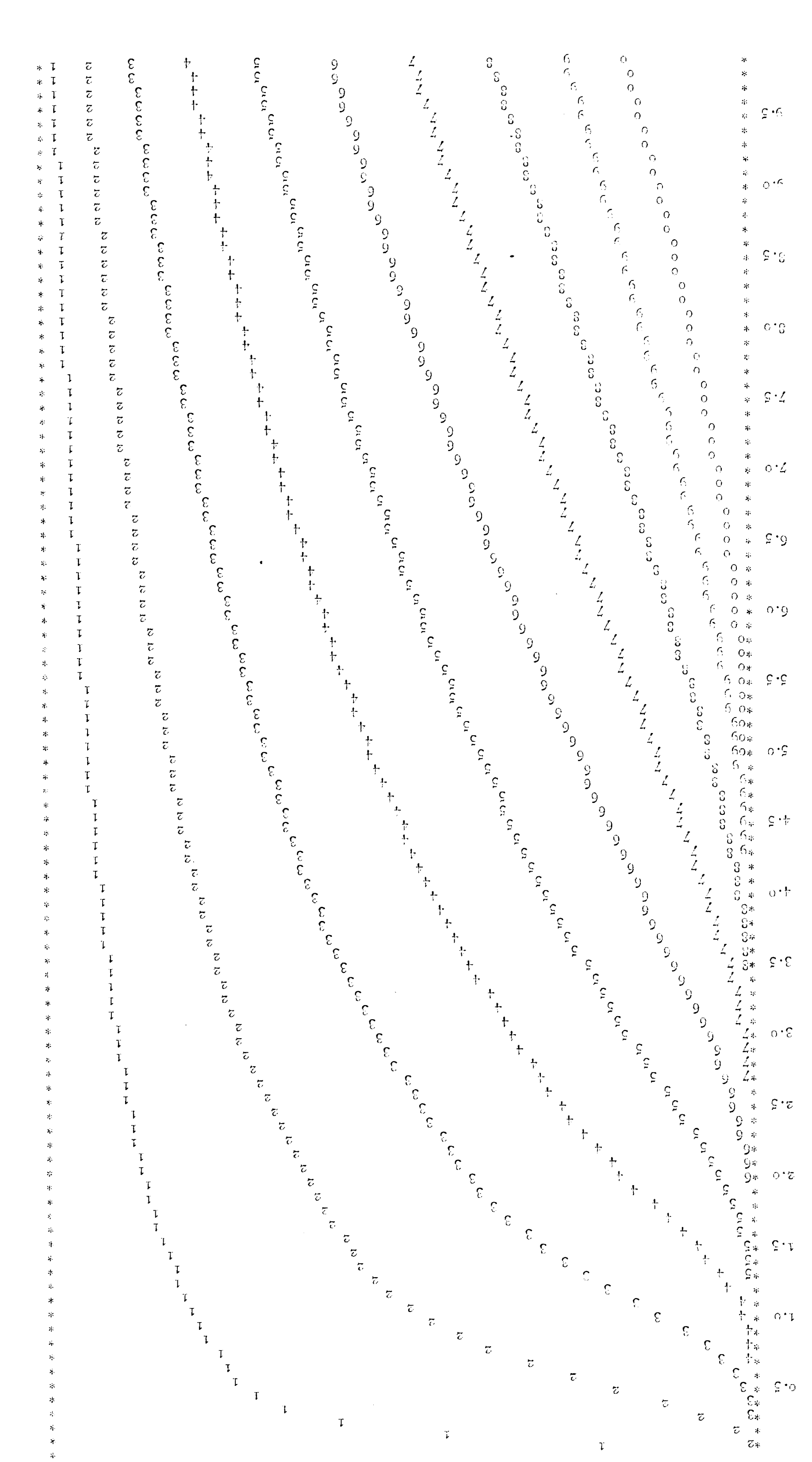
COMPUTER RUN NUMBER 1 C

PROGRAMME PARAMETERS

BED RESIDENCE TIME	(Z)=	30.20
PELLET RESISTANCE	(X)=	57.60
CRYSTAL RESISTANCE	(Y)=	350.00
PELLET SHAPE FACTOR (ALPHA)=		1.85

FINITE-DIFFERENCE PARAMETERS

NUMBER OF STEPS IN BED LENGTH	(Q)=	10
NUMBER OF STEPS IN PELLET RADIUS (R)=		5
NUMBER OF STEPS IN CRYSTAL RADIUS(S)=		4
NUMBER OF MINUTES IN TIME-STEP (T)=		1.2

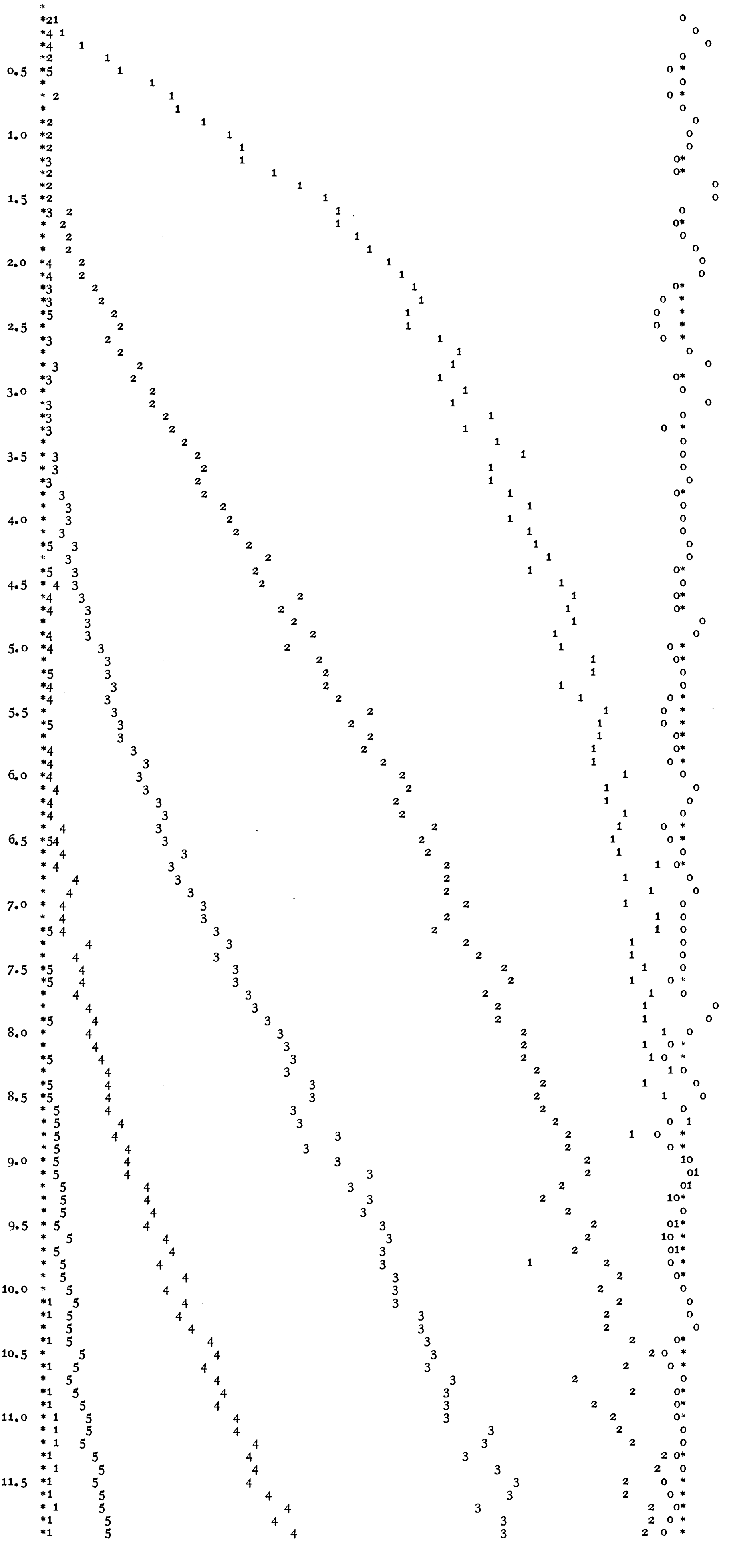


PLOT OF EXPERIMENTAL BREAKTHROUGH CURVES

EXPERIMENT NUMBER 2 A

EXPERIMENTAL CONDITIONS

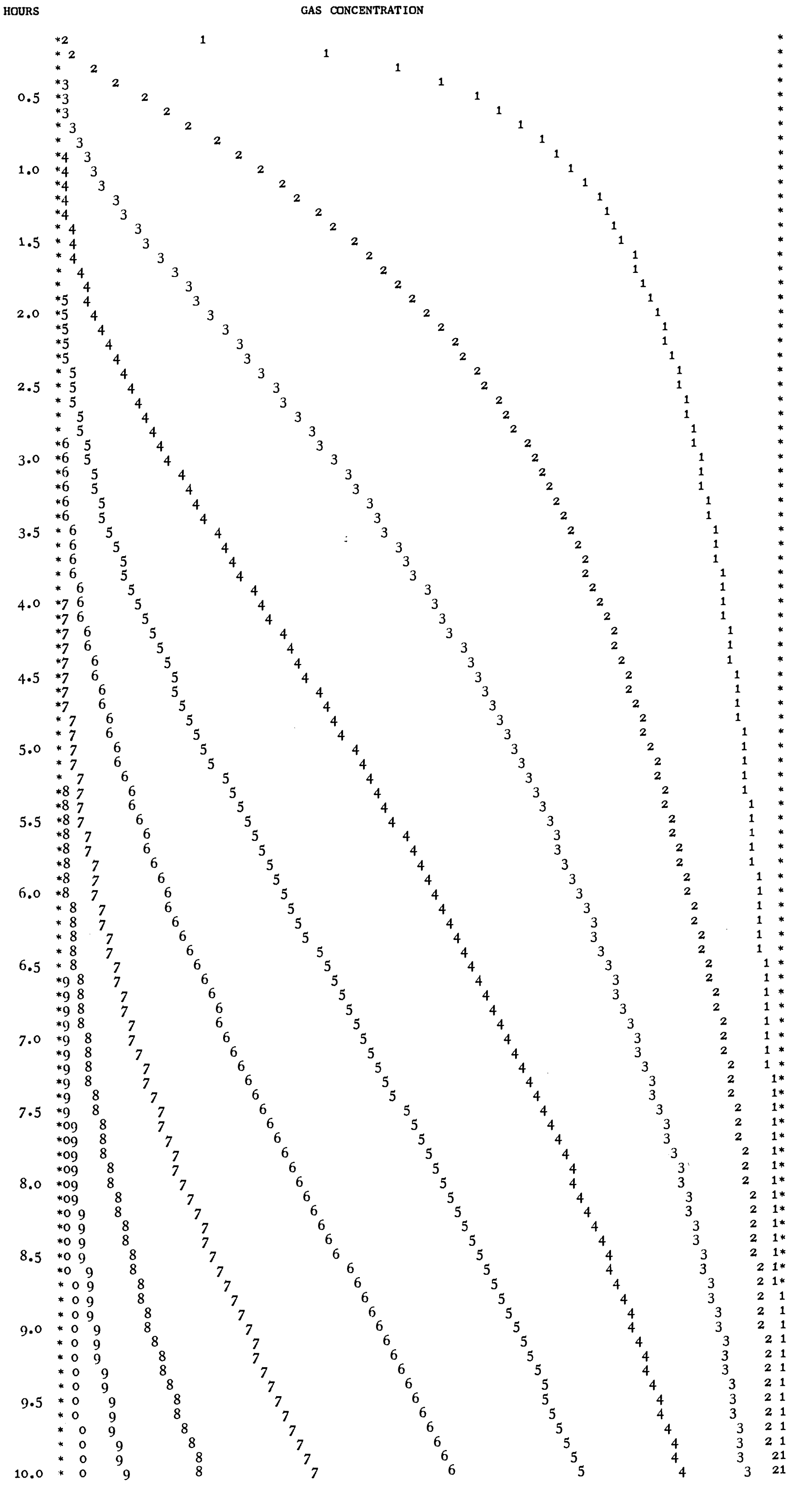
MOLECULAR SIEVE TYPE 5A,1/8 INCH DIAMETER CYLINDERS
PRESSURE, 12.50 ATMOSPHERES ABSOLUTE
TEMPERATURE, 0.8 DEGREES CELSIUS
AIR FLOW RATE, 7.50 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 492 PARTS PER MILLION OF CO2



PLOT OF COMPUTED BREAKTHROUGH CURVES

COMPUTER RUN NUMBER 2 C

PROGRAMME PARAMETERS		FINITE-DIFFERENCE PARAMETERS	
BED RESIDENCE TIME (E)=	30.20	NUMBER OF STEPS IN BED LENGTH (Q)=	10
PELLET RESISTANCE (X)=	28.80	NUMBER OF STEPS IN PELLET RADIUS (R)=	9
CRYSTAL RESISTANCE (Y)=	350.00	NUMBER OF STEPS IN CRYSTAL RADIUS(S)=	4
PELLET SHAPE FACTOR (ALPHA)=	1.83	NUMBER OF MINUTES IN TIME-STEP (T)=	1.2

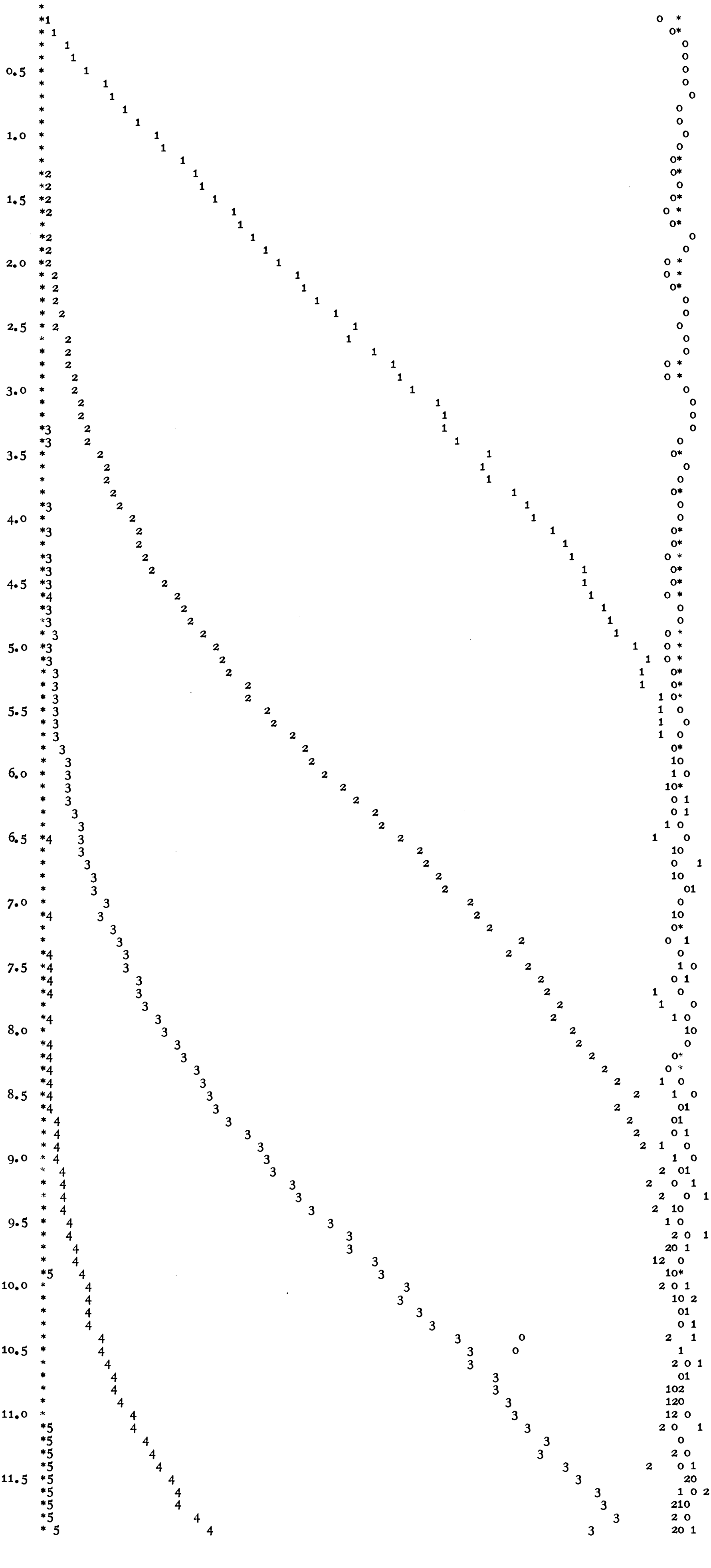


PLOT OF EXPERIMENTAL BREAKTHROUGH CURVES

EXPERIMENT NUMBER 3 A

EXPERIMENTAL CONDITIONS

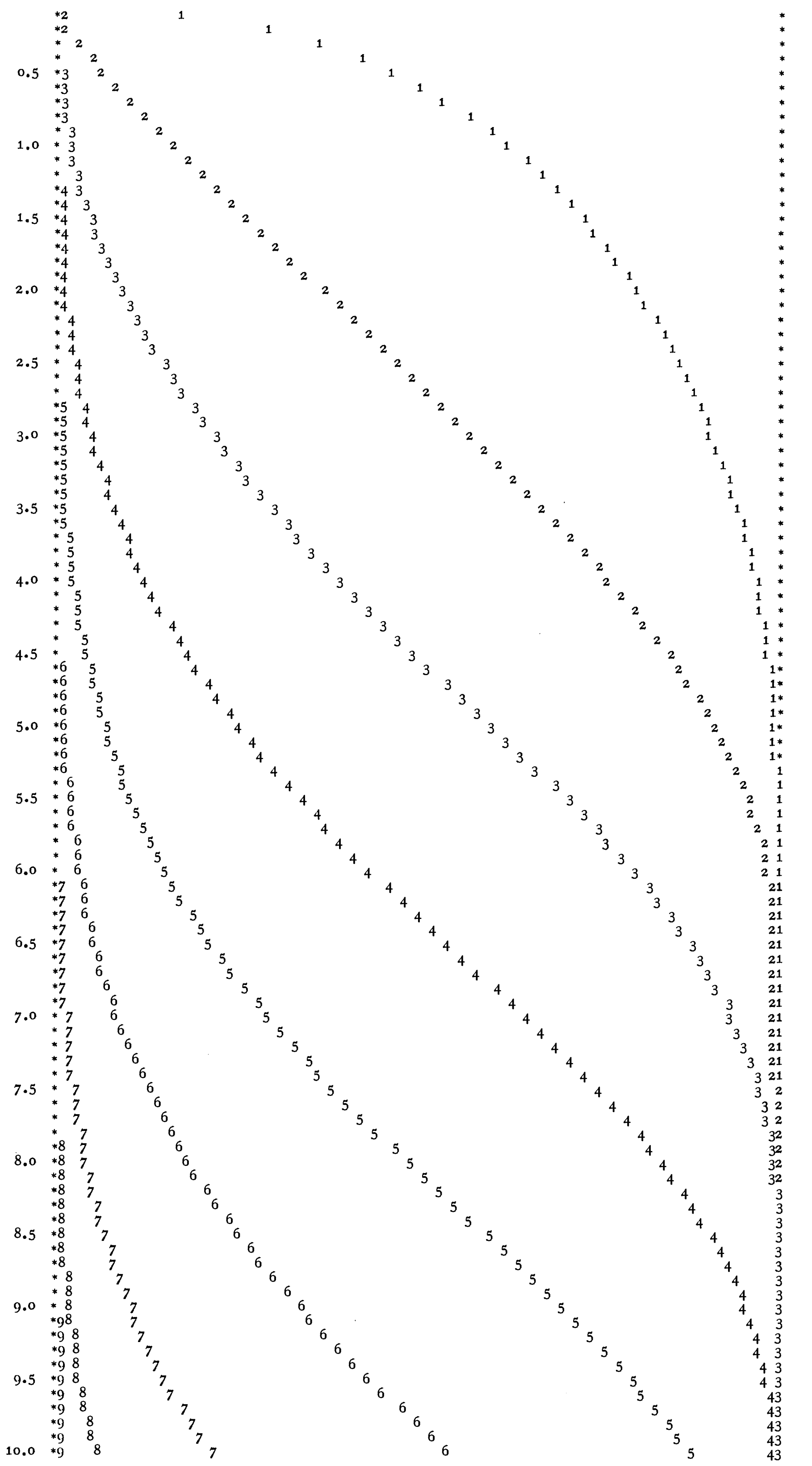
MOLECULAR SIEVE TYPE 5A, 1/8 INCH DIAMETER CYLINDERS
PRESSURE, 6.25 ATMOSPHERES ABSOLUTE
TEMPERATURE, -2.1 DEGREES CELSIUS
AIR FLOW RATE, 3.75 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 998 PARTS PER MILLION OF CO2



PLOT OF COMPUTED BREAKTHROUGH CURVES

COMPUTER RUN NUMBER 3 C

PROGRAMME PARAMETERS		FINITE-DIFFERENCE PARAMETERS	
BED RESIDENCE TIME (E)=	30.20	NUMBER OF STEPS IN BED LENGTH (Q)=	10
PELLET RESISTANCE (X)=	14.40	NUMBER OF STEPS IN PELLET RADIUS (R)=	9
CRYSTAL RESISTANCE (Y)=	350.00	NUMBER OF STEPS IN CRYSTAL RADIUS(S)=	4
PELLET SHAPE FACTOR (ALPHA)=	1.83	NUMBER OF MINUTES IN TIME-STEP (T)=	1.2

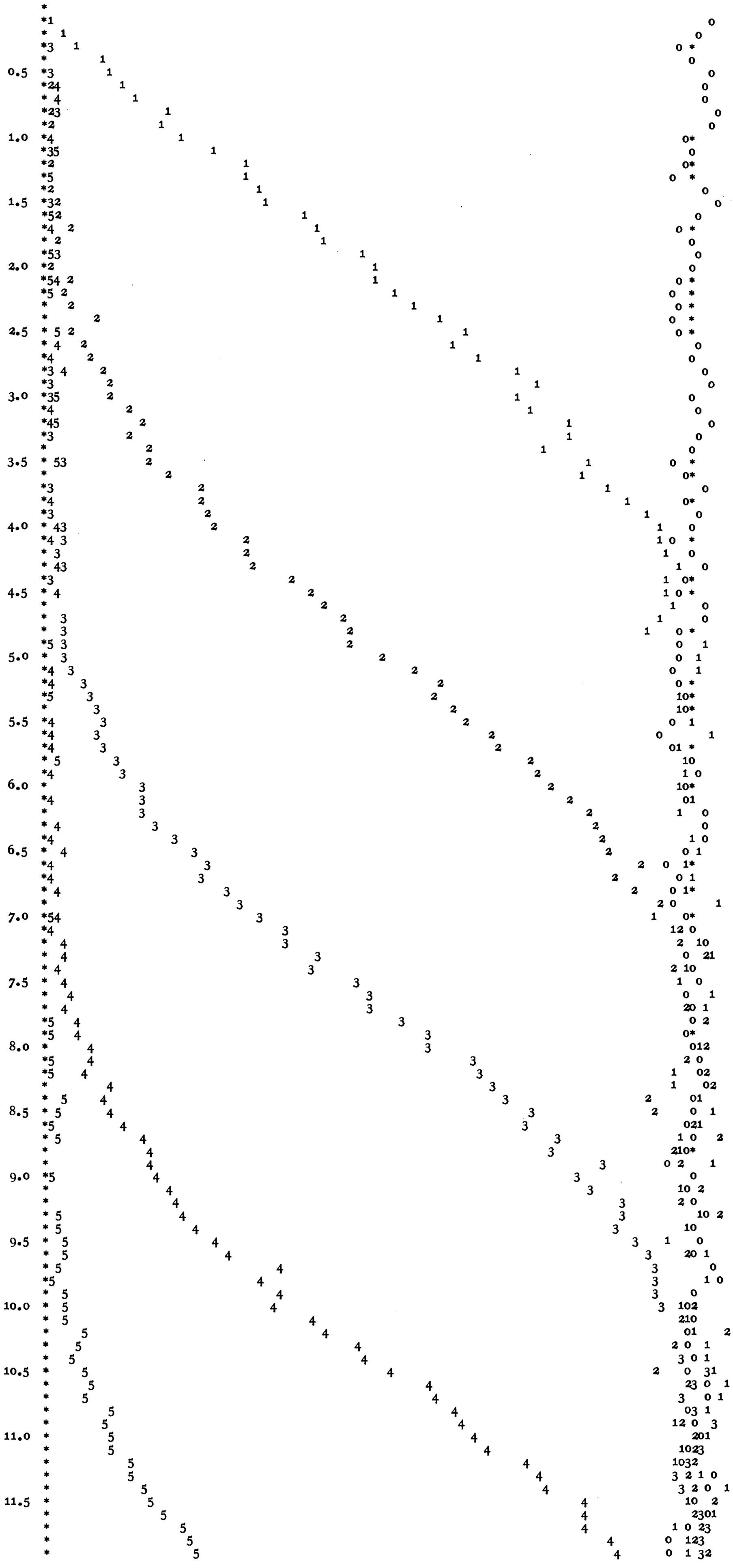


PLOT OF EXPERIMENTAL BREAKTHROUGH CURVES

EXPERIMENT NUMBER 4 A

EXPERIMENTAL CONDITIONS

MOLECULAR SIEVE TYPE 5A,1/16 INCH DIAMETER CYLINDERS
PRESSURE, 25.00 ATMOSPHERES ABSOLUTE
TEMPERATURE, 1.2 DEGREES CELSIUS
AIR FLOW RATE, 15.00 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 245 PARTS PER MILLION OF CO2



PLOT OF COMPUTED BREAKTHROUGH CURVES

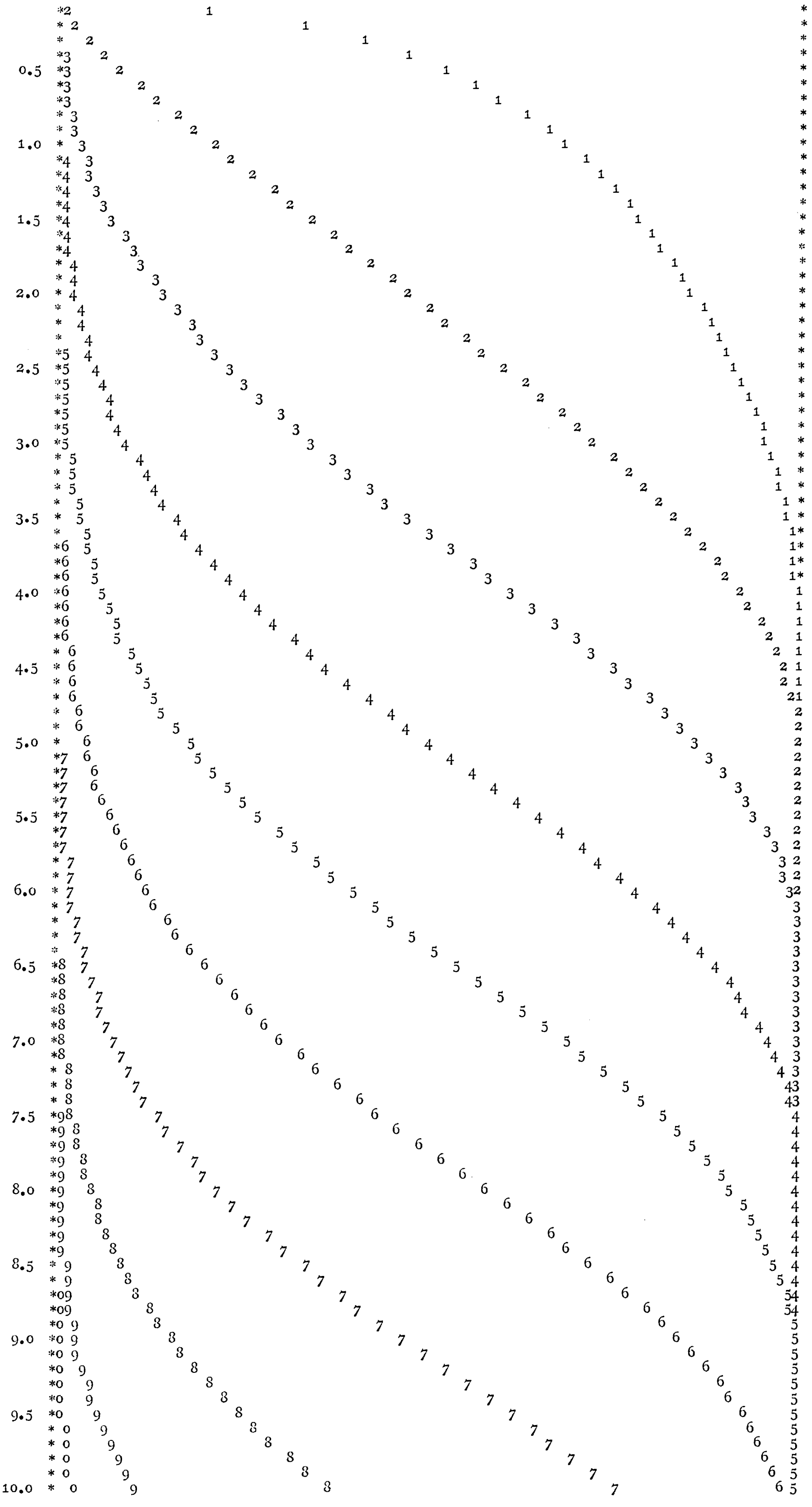
COMPUTER RUN NUMBER 4 C

PROGRAMME PARAMETERS

BED RESIDENCE TIME (E)= 30.20
PELLET RESISTANCE (X)= 14.40
CRYSTAL RESISTANCE (Y)= 350.00
PELLET SHAPE FACTOR (ALPHA)= 1.55

FINITE-DIFFERENCE PARAMETERS

NUMBER OF STEPS IN BED LENGTH (Q)= 10
NUMBER OF STEPS IN PELLET RADIUS (R)= 9
NUMBER OF STEPS IN CRYSTAL RADIUS(S)= 4
NUMBER OF MINUTES IN TIME-STEP (T)= 1.2

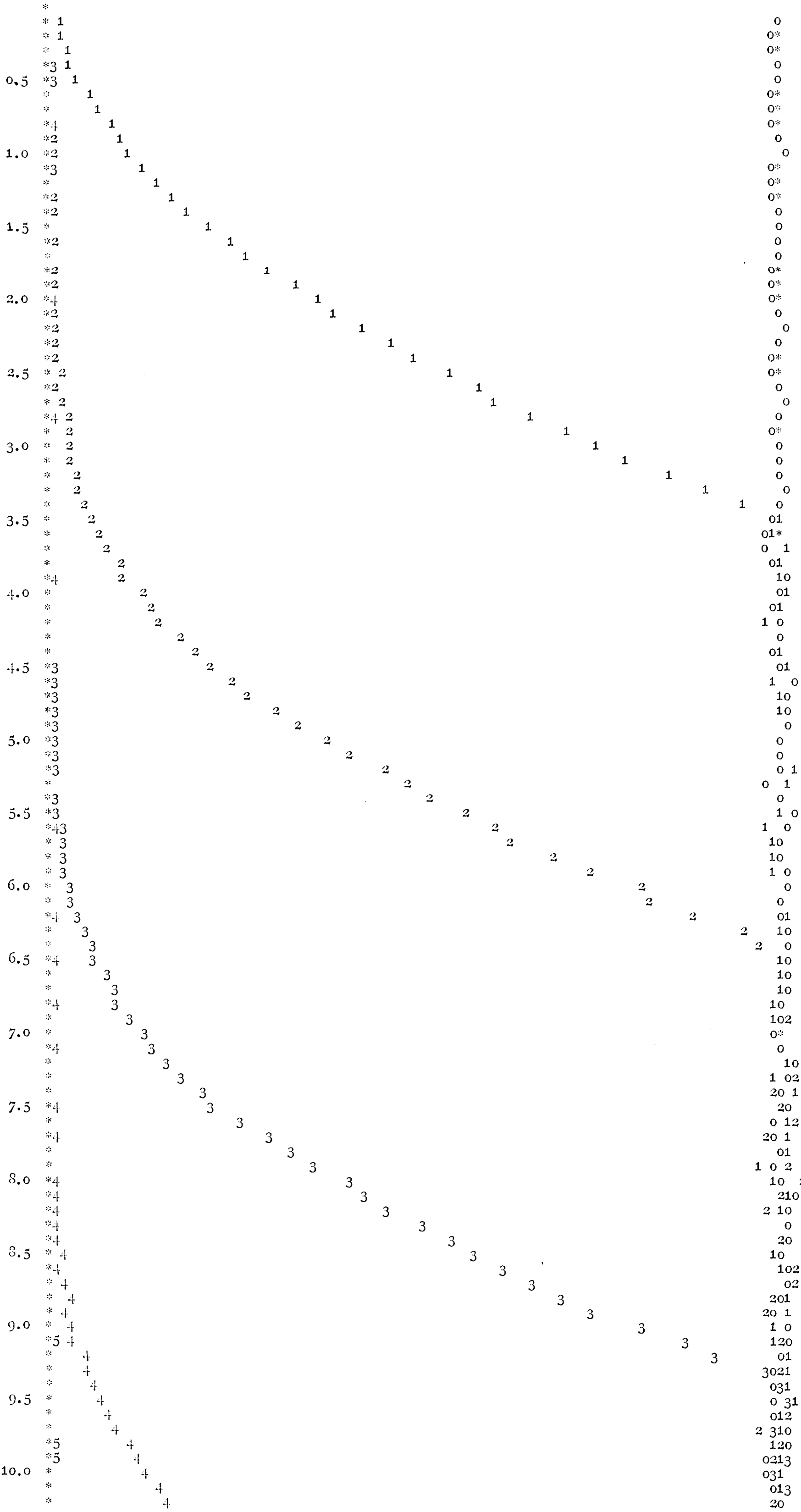


PLOT OF EXPERIMENTAL BREAKTHROUGH CURVES

EXPERIMENT NUMBER 5 A

EXPERIMENTAL CONDITIONS

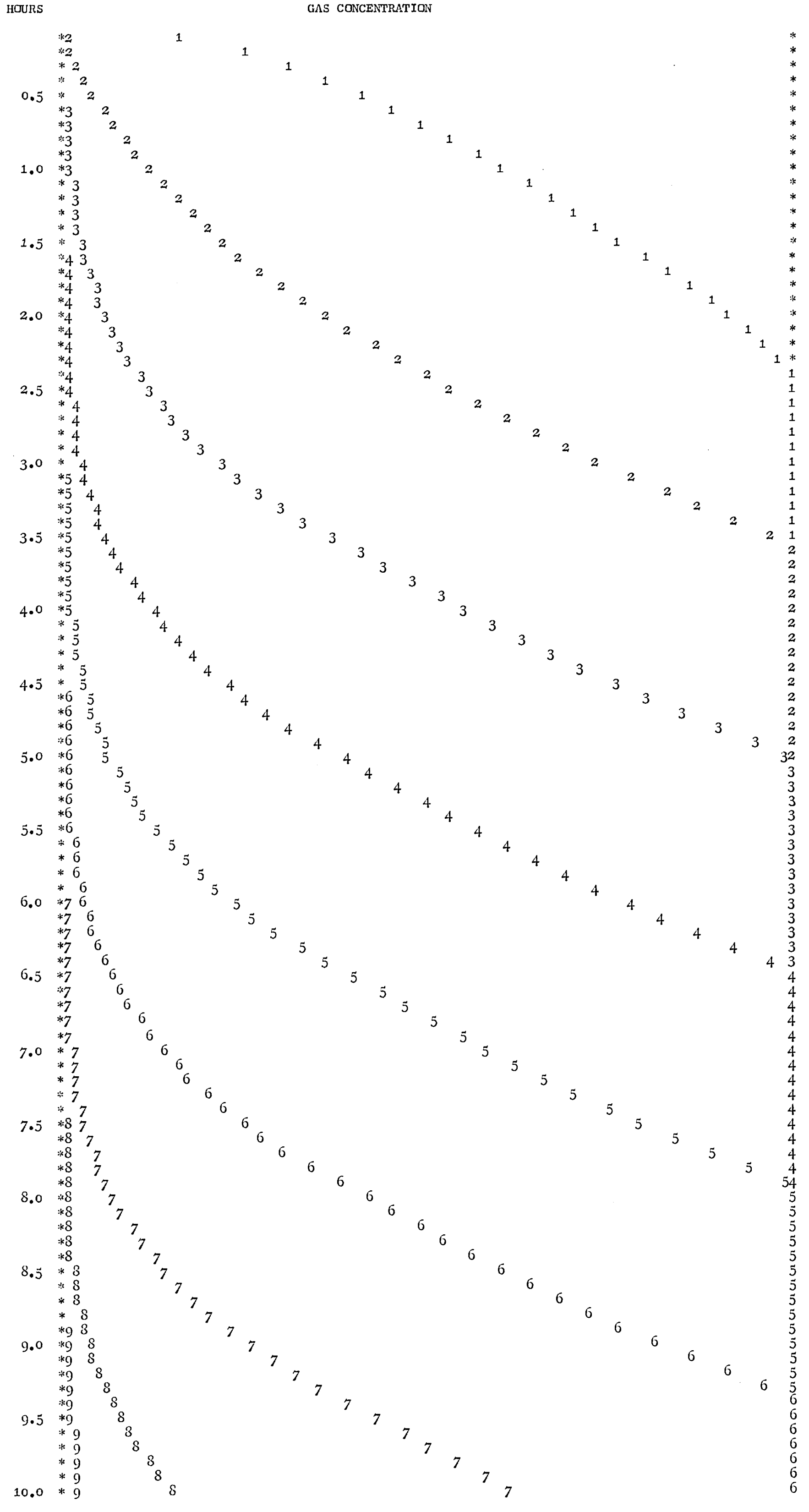
MOLECULAR SIEVE TYPE 5A,1/16 INCH DIAMETER CYLINDERS
PRESSURE, 12.50 ATMOSPHERES ABSOLUTE
TEMPERATURE, -0.6 DEGREES CELSIUS
AIR FLOW RATE, 7.50 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 499 PARTS PER MILLION OF CO2



PLOT OF COMPUTED BREAKTHROUGH CURVES

COMPUTER RUN NUMBER 5 C

PROGRAMME PARAMETERS		FINITE-DIFFERENCE PARAMETERS	
BED RESIDENCE TIME	(E)= 30.20	NUMBER OF STEPS IN BED LENGTH	(Q)= 10
PELLET RESISTANCE	(X)= 7.20	NUMBER OF STEPS IN PELLET RADIUS	(R)= 9
CRYSTAL RESISTANCE	(Y)= 350.00	NUMBER OF STEPS IN CRYSTAL RADIUS	(S)= 4
PELLET SHAPE FACTOR (ALPHA)	= 1.55	NUMBER OF MINUTES IN TIME-STEP	(T)= 1.2

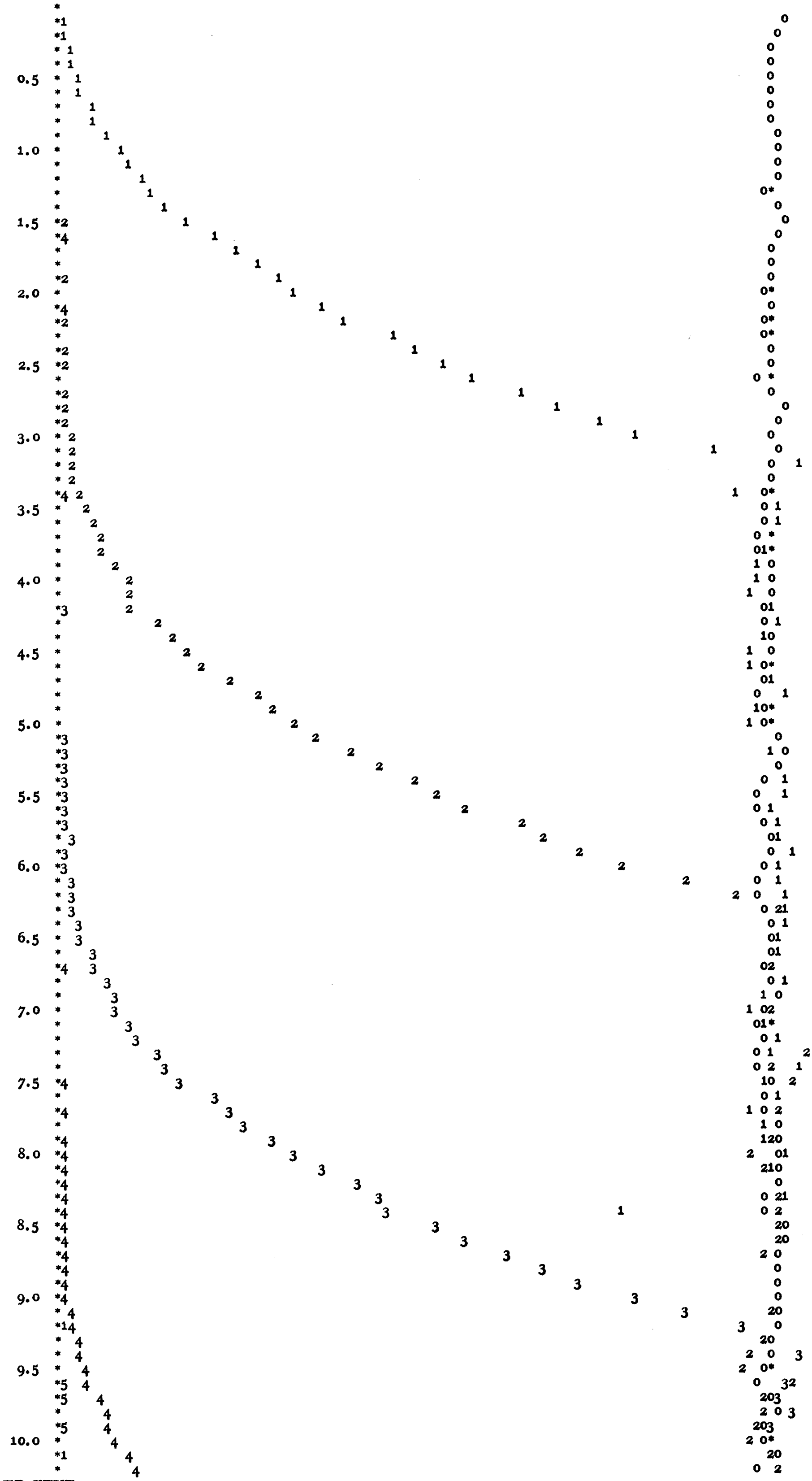


PLOT OF EXPERIMENTAL BREAKTHROUGH CURVES

EXPERIMENT NUMBER 6 A

EXPERIMENTAL CONDITIONS

MOLECULAR SIEVE TYPE 5A,1/16 INCH DIAMETER CYLINDERS
PRESSURE, 6.25 ATMOSPHERES ABSOLUTE
TEMPERATURE, -1.5 DEGREES CELSIUS
AIR FLOW RATE, 3.75 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 998 PARTS PER MILLION OF CO2



END OUTPUT

PLOT OF COMPUTED BREAKTHROUGH CURVES

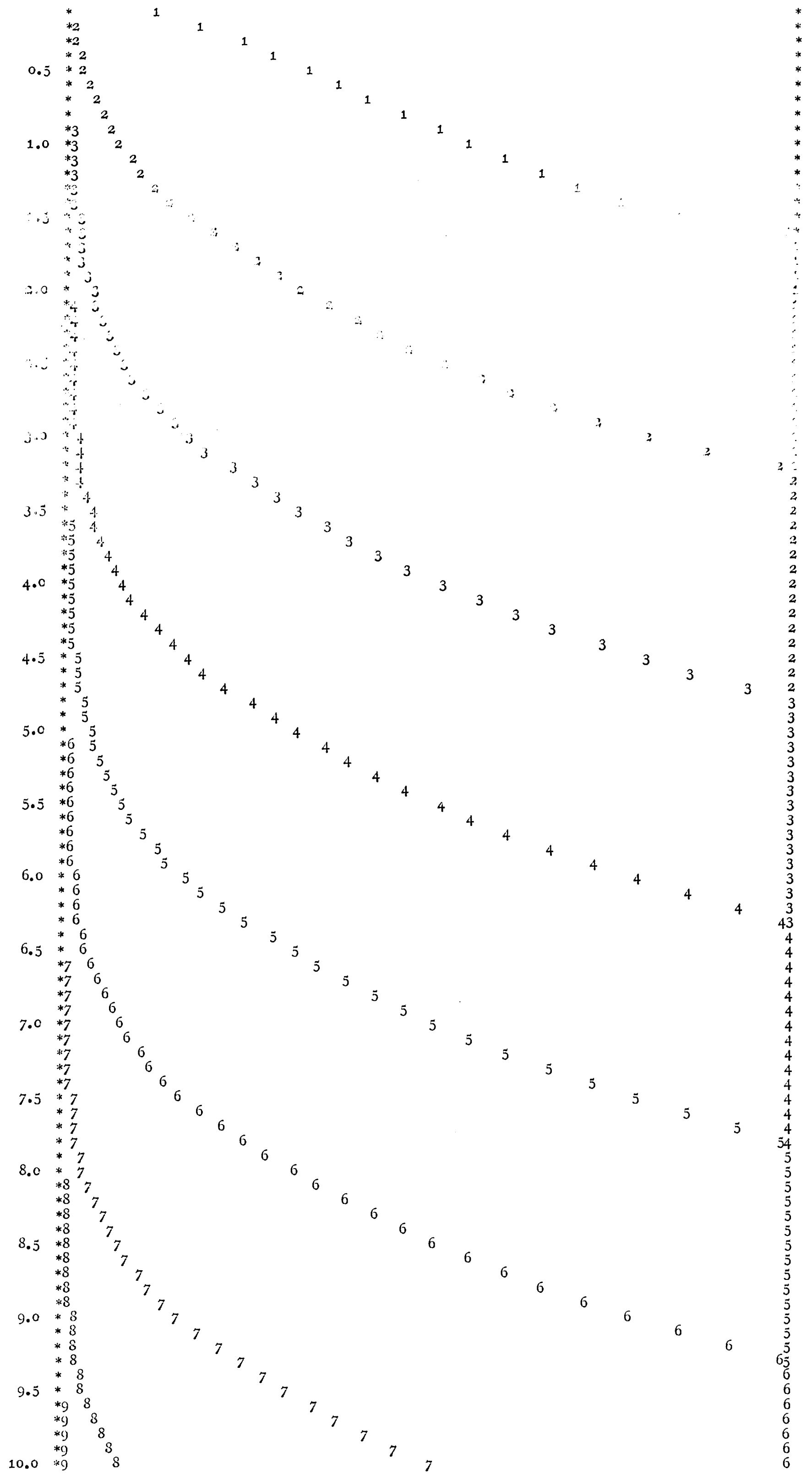
COMPUTER RUN NUMBER 6 C

PROGRAMME PARAMETERS

BED RESIDENCE TIME (E)= 30.20
PELLET RESISTANCE (X)= 3.60
CRYSTAL RESISTANCE (Y)= 350.00
PELLET SHAPE FACTOR (ALPHA)= 1.55

FINITE-DIFFERENCE PARAMETERS

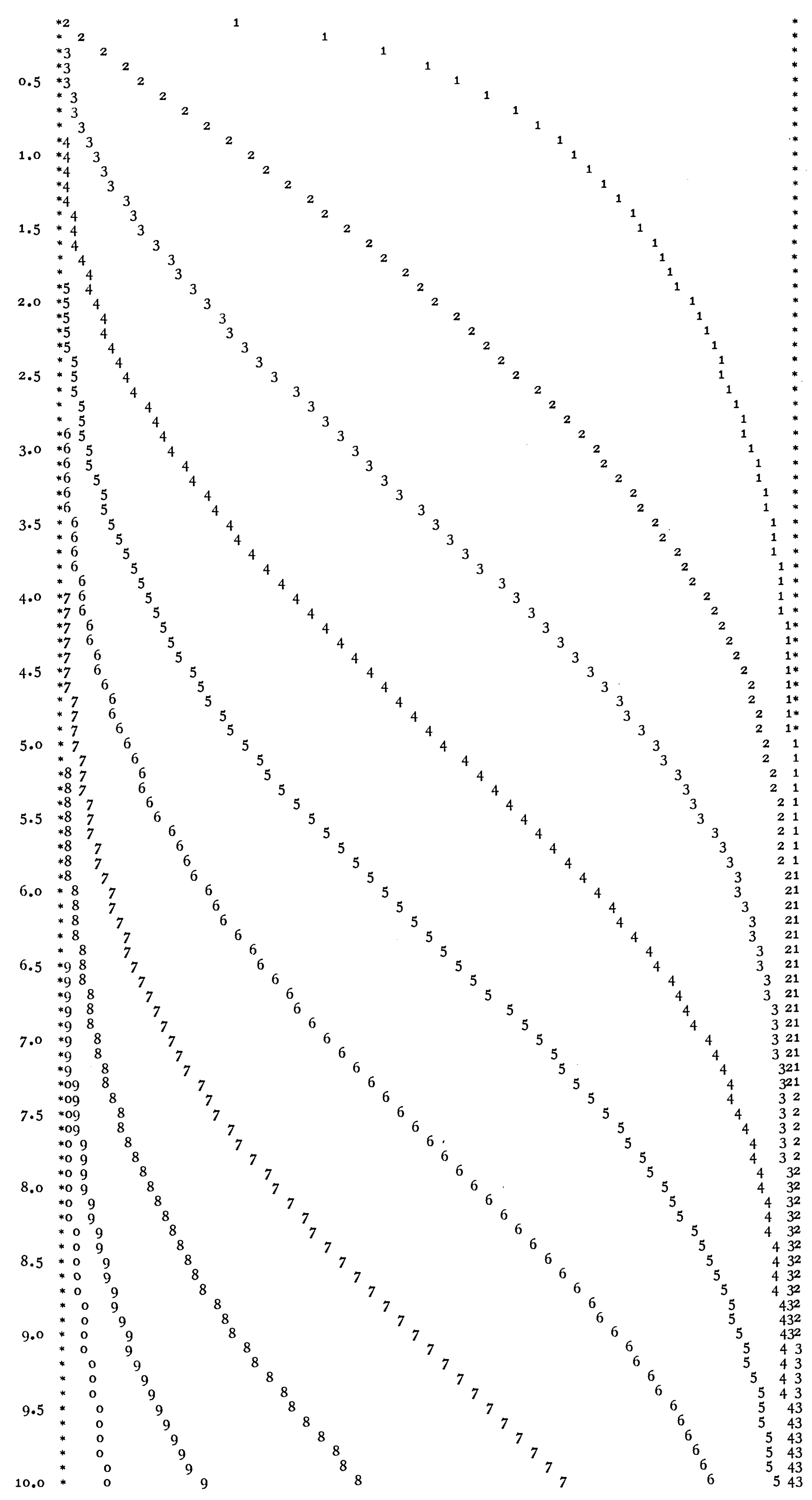
NUMBER OF STEPS IN BED LENGTH (Q)= 10
NUMBER OF STEPS IN PELLET RADIUS (R)= 9
NUMBER OF STEPS IN CRYSTAL RADIUS(S)= 4
NUMBER OF MINUTES IN TIME-STEP (T)= 1.2



PLOT OF COMPUTED BREAKTHROUGH CURVES

COMPUTER RUN NUMBER 7 C

PROGRAMME PARAMETERS		FINITE-DIFFERENCE PARAMETERS	
BED RESIDENCE TIME (E)=	30.20	NUMBER OF STEPS IN BED LENGTH (Q)=	10
PELLET RESISTANCE (X)=	14.40	NUMBER OF STEPS IN PELLET RADIUS (R)=	9
CRYSTAL RESISTANCE (Y)=	350.00	NUMBER OF STEPS IN CRYSTAL RADIUS(S)=	4
PELLET SHAPE FACTOR (ALPHA)=	1.55	NUMBER OF MINUTES IN TIME-STEP (T)=	1.2



PLOT OF COMPUTED BREAKTHROUGH CURVES

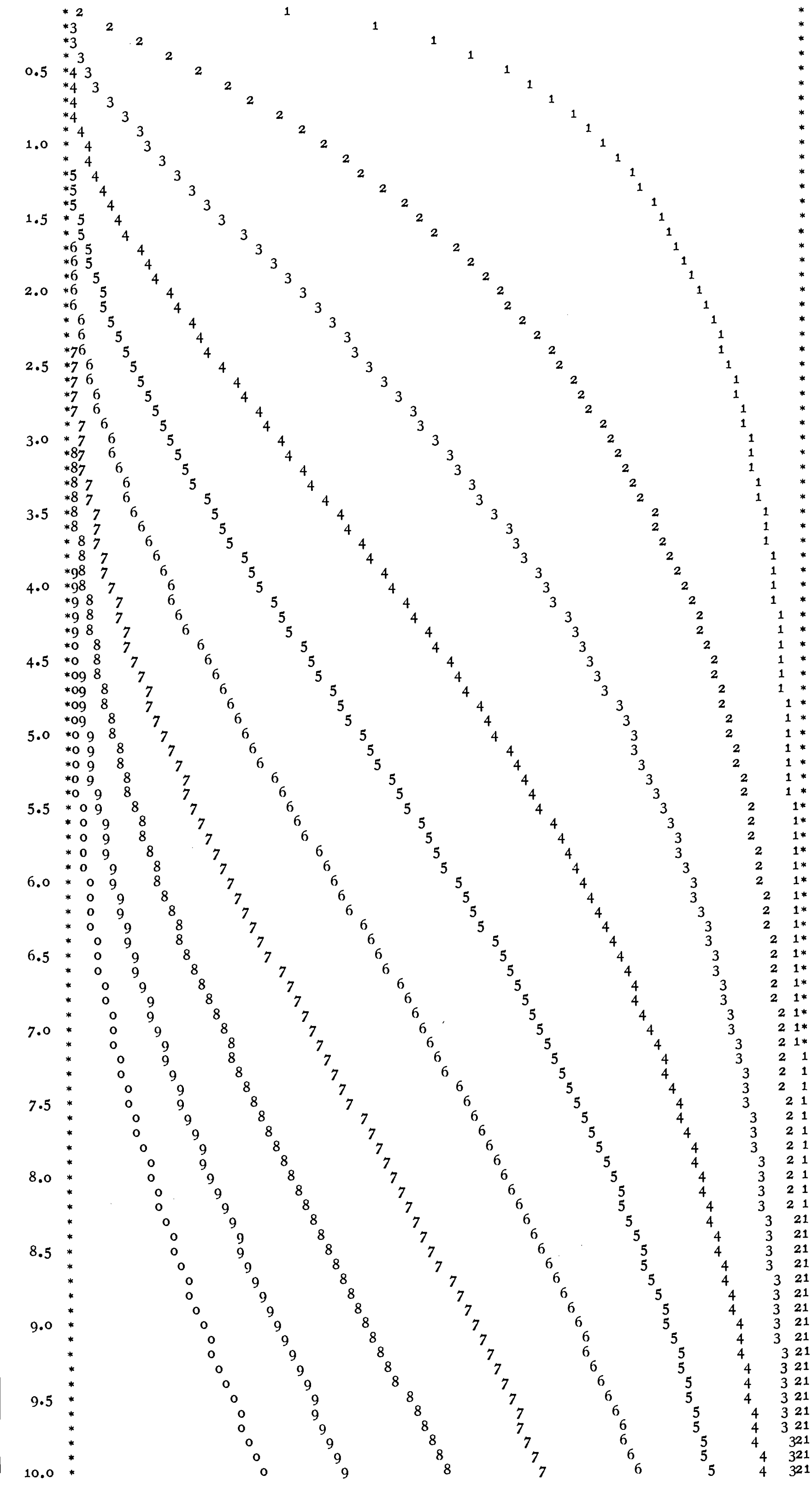
COMPUTER RUN NUMBER 8 C

PROGRAMME PARAMETERS

BED RESIDENCE TIME (E)= 30.20
PELLET RESISTANCE (X)= 14.40
CRYSTAL RESISTANCE (Y)= 350.00
PELLET SHAPE FACTOR (ALPHA)= 1.55

FINITE-DIFFERENCE PARAMETERS

NUMBER OF STEPS IN BED LENGTH (Q)= 10
NUMBER OF STEPS IN PELLET RADIUS (R)= 9
NUMBER OF STEPS IN CRYSTAL RADIUS(S)= 4
NUMBER OF MINUTES IN TIME-STEP (T)= 1.2

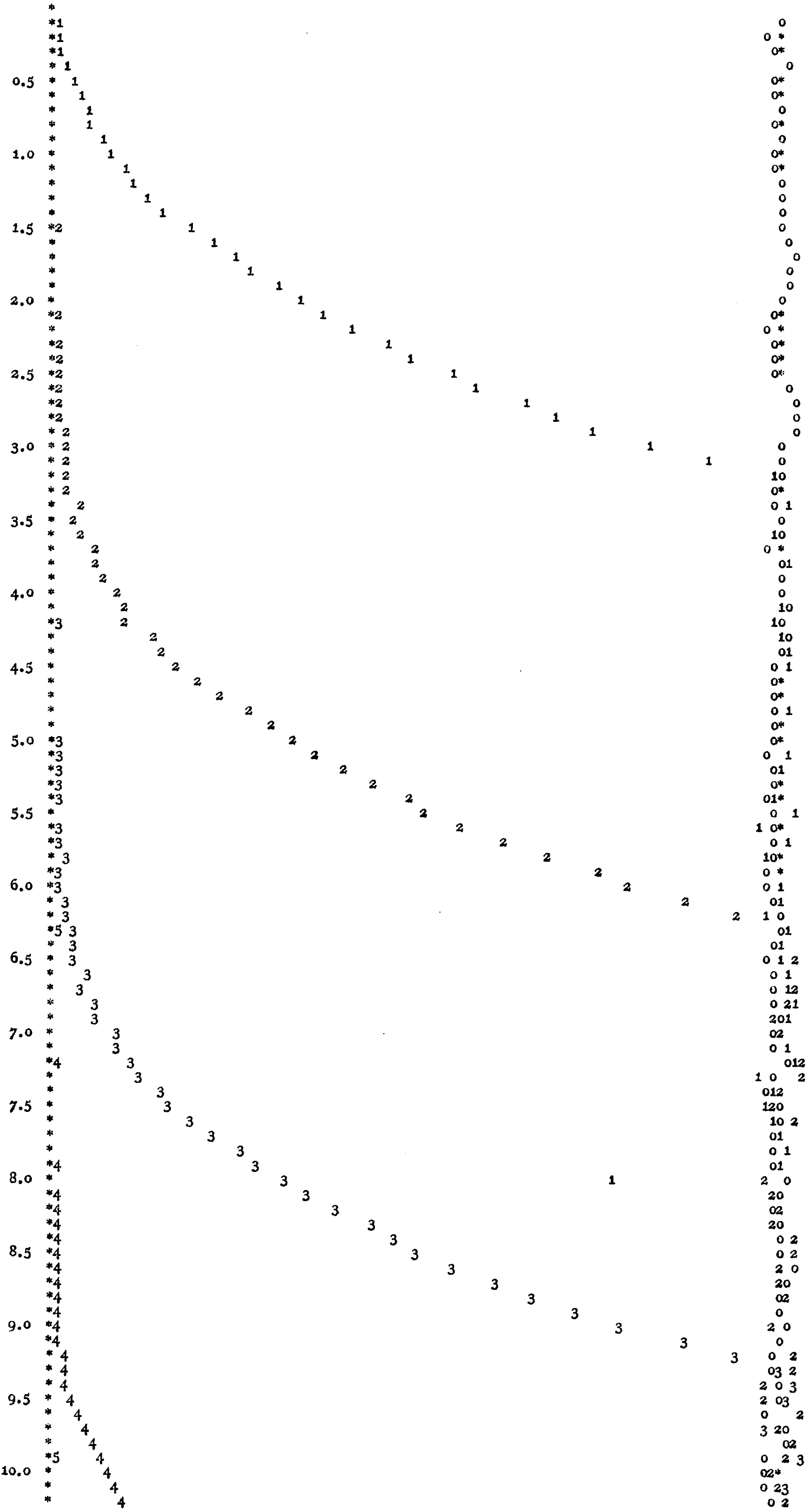


PLOT OF EXPERIMENTAL BREAKTHROUGH CURVES

EXPERIMENT NUMBER 1 B

EXPERIMENTAL CONDITIONS

MOLECULAR SIEVE TYPE 5A,1/16 INCH DIAMETER CYLINDERS
PRESSURE, 6.25 ATMOSPHERES ABSOLUTE
TEMPERATURE, 0.7 DEGREES CELSIUS
AIR FLOW RATE, 3.75 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 996 PARTS PER MILLION OF CO2

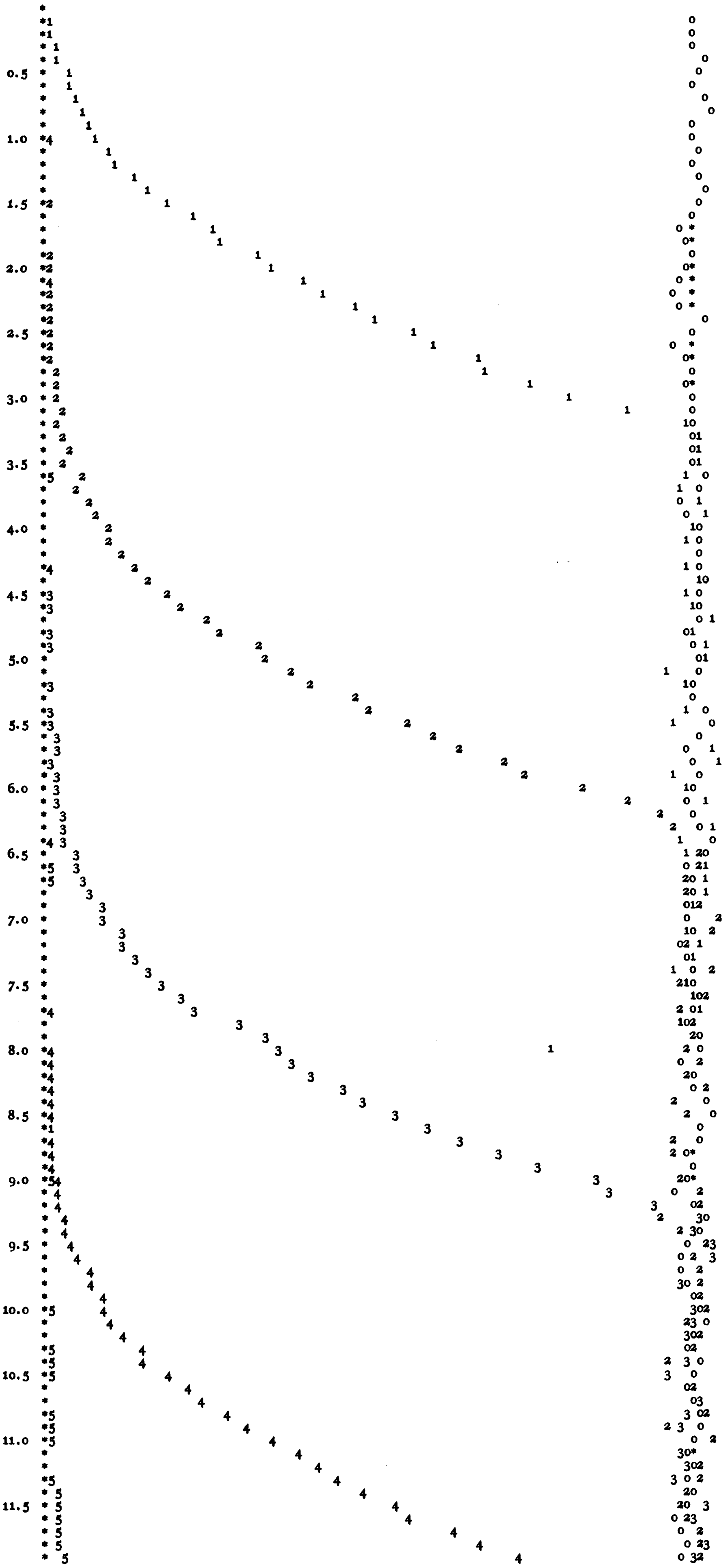


PLOT OF EXPERIMENTAL BREAKTHROUGH CURVES

EXPERIMENT NUMBER 2 B

EXPERIMENTAL CONDITIONS

MOLECULAR SIEVE TYPE 5A, 1/16 INCH DIAMETER CYLINDERS
PRESSURE, 6.25 ATMOSPHERES ABSOLUTE
TEMPERATURE, 1.7 DEGREES CELSIUS
AIR FLOW RATE, 3.75 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 999 PARTS PER MILLION OF CO2

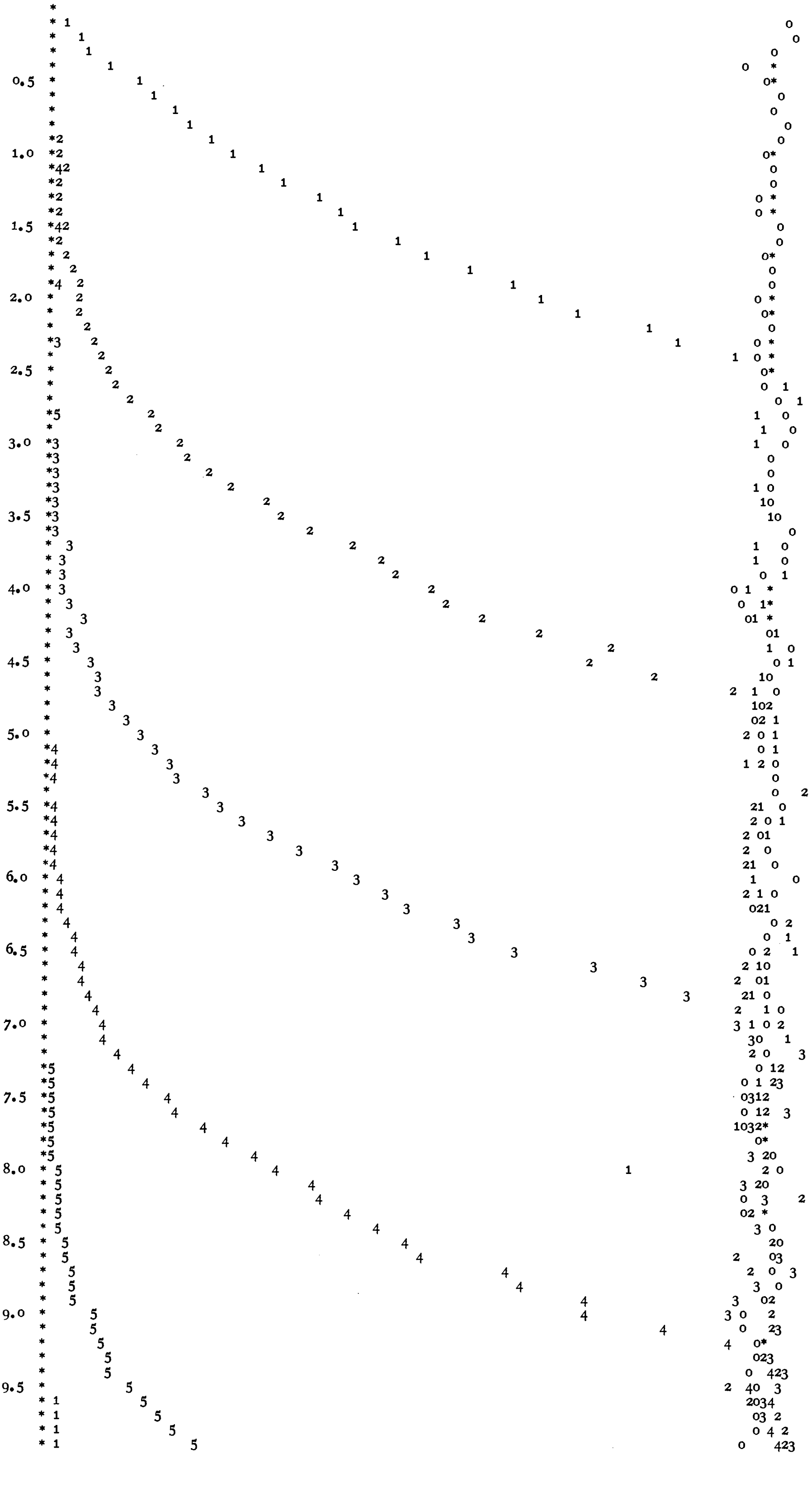


PLOT OF EXPERIMENTAL BREAKTHROUGH CURVES

EXPERIMENT NUMBER 3 B

EXPERIMENTAL CONDITIONS

MOLECULAR SIEVE TYPE 5A, 1/16 INCH DIAMETER CYLINDERS
PRESSURE, 6.25 ATMOSPHERES ABSOLUTE
TEMPERATURE, -0.3 DEGREES CELSIUS
AIR FLOW RATE, 5.00 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 1010 PARTS PER MILLION OF CO2

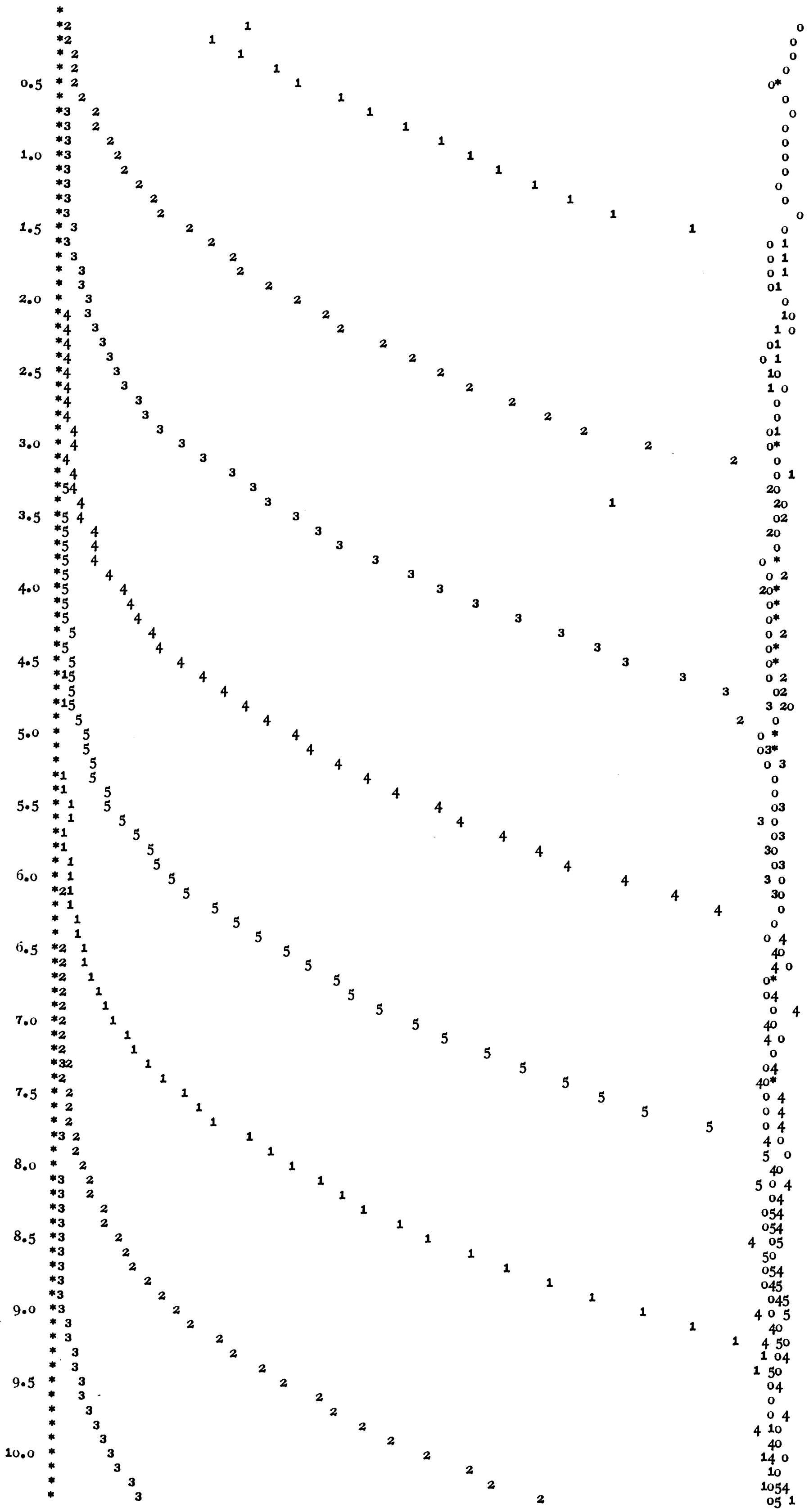


PLOT OF EXPERIMENTAL BREAKTHROUGH CURVES

EXPERIMENT NUMBER 4 B

EXPERIMENTAL CONDITIONS

MOLECULAR SIEVE TYPE 5A,1/16 INCH DIAMETER CYLINDERS
PRESSURE, 6.25 ATMOSPHERES ABSOLUTE
TEMPERATURE, -2.3 DEGREES CELSIUS
AIR FLOW RATE, 7.50 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 1004 PARTS PER MILLION OF CO2

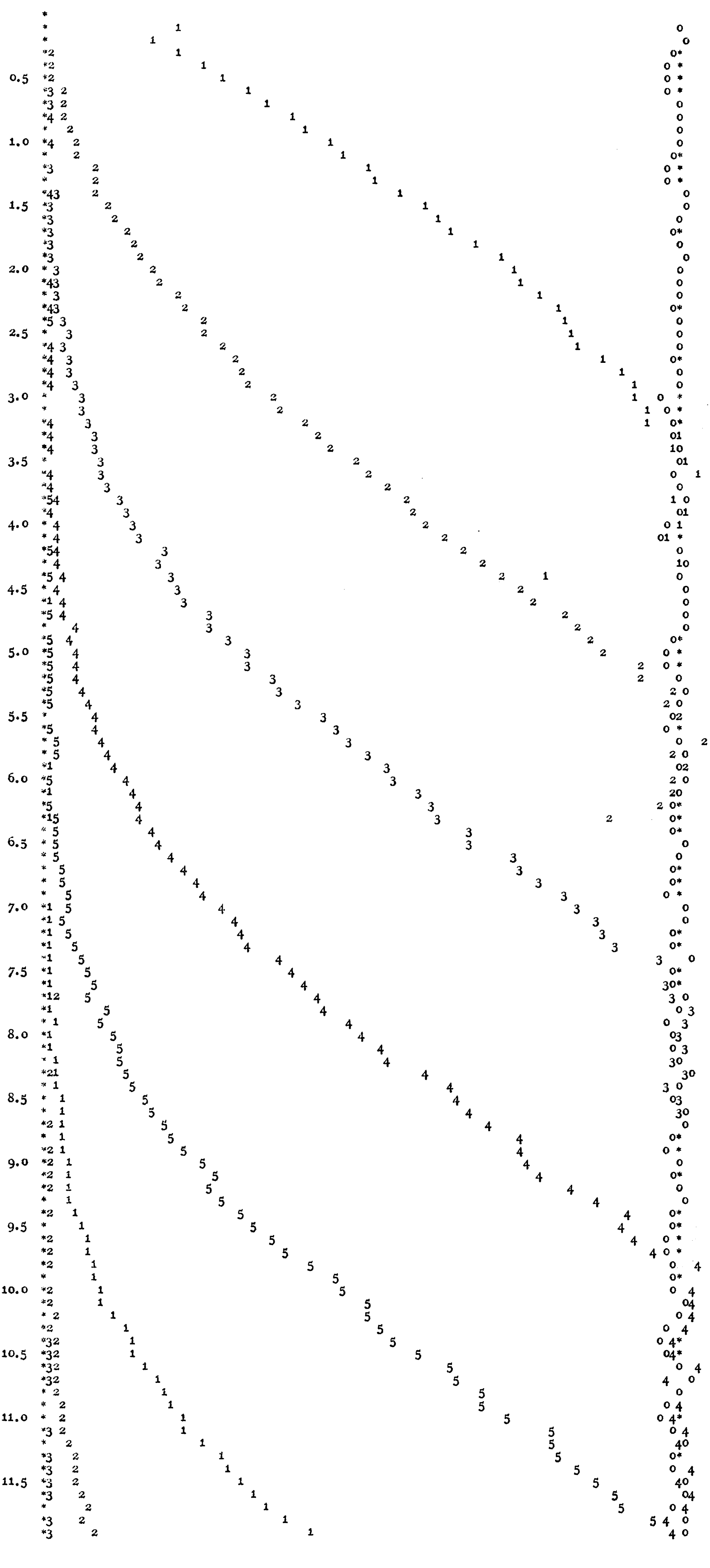


PLOT OF EXPERIMENTAL BREAKTHROUGH CURVES

EXPERIMENT NUMBER 5 B

EXPERIMENTAL CONDITIONS

MOLECULAR SIEVE TYPE 5A,1/16 INCH DIAMETER CYLINDERS
PRESSURE, 6.25 ATMOSPHERES ABSOLUTE
TEMPERATURE, 0.9 DEGREES CELSIUS
AIR FLOW RATE, 7.50 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 501 PARTS PER MILLION OF CO2

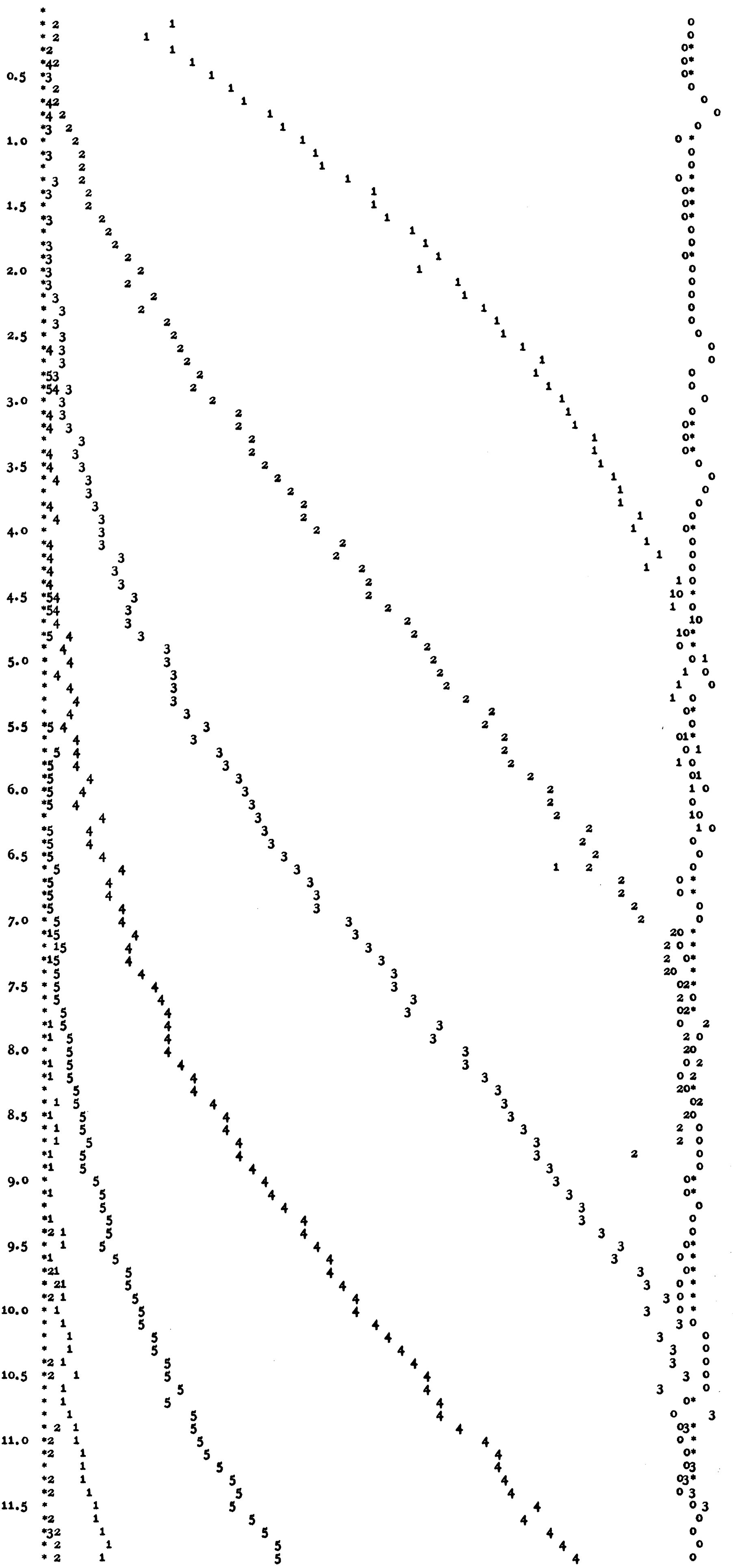


PLOT OF EXPERIMENTAL BREAKTHROUGH CURVES

EXPERIMENT NUMBER 6 B

EXPERIMENTAL CONDITIONS

MOLECULAR SIEVE TYPE 5A,1/16 INCH DIAMETER CYLINDERS
PRESSURE, 6.25 ATMOSPHERES ABSOLUTE
TEMPERATURE, 1.3 DEGREES CELSIUS
AIR FLOW RATE, 7.50 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 253 PARTS PER MILLION OF CO2



TABULATION OF 1000C/CO AS A FUNCTION OF TIME AND BED LENGTH

EXPERIMENT NUMBER 1 A

EXPERIMENTAL CONDITIONS

MOLECULAR SIEVE TYPE 5A,1/8 INCH DIAMETER CYLINDERS
PRESSURE, 25.00 ATMOSPHERES ABSOLUTE
TEMPERATURE, 1.4 DEGREES CELSIUS
AIR FLOW RATE, 15.00 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 249 PARTS PER MILLION OF CO2

SAMPLE POINT NO.	0	1	2	3	4	5	6	7	8
TIME OF SAMPLE	T	T+1	T+2	T+3	T+4	T+5	T+1	T+2	T+3
ELAPSED TIME (T) IN MINUTES									
0	998	0	0	22	0	0			
6	975	22	0	11	0	0			
12	1035	84	0	0	11	0			
18	1005	123	0	0	5	0			
24	1016	181	0	0	9	11			
30	996	252	24	0	0	7			
36	971	322	13	0	18	3			
42	981	378	11	0	0	0			
48	994	391	3	0	9	0			
54	994	451	41	0	0	0			
60	1007	492	18	0	3	15			
66	962	498	22	0	0	0			
72	1007	541	56	0	3	0			
78	986	528	71	9	3	3			
84	996	548	69	3	0	0			
90	986	571	88	0	0	0			
96	1011	601	112	13	5	0			
102	994	614	134	3	0	5			
108	1018	584	157	0	11	13			
114	947	636	159	0	0	3			
120	975	616	176	13	13	0			
126	992	640	196	9	0	0			
132	1001	672	230	5	0	0			
138	1022	683	269	5	0	0			
144	1026	689	256	35	0	0			
150	962	696	264	0	0	5			
156	988	670	282	39	0	0			
162	962	704	307	52	0	11			
168	975	715	327	63	0	3			
174	1022	719	320	54	3	0			
180	953	698	355	76	0	0			
186	1022	760	342	69	9	5			
192	1005	724	350	69	0	0			
198	1003	745	363	99	11	0			
204	983	760	400	108	9	0			
210	1035	750	391	121	11	0			
216	981	771	419	103	0	26			
222	1005	792	404	149	7	0			
228	1016	767	415	112	18	18			
234	1061	777	458	138	13	0			
240	988	801	434	153	24	0			
246	1005	775	443	189	9	0			
252	1016	801	470	144	7	5			
258	979	784	477	194	26	0			
264	1003	792	453	174	35	11			
270	981	795	488	198	24	0			
276	996	833	486	183	15	9			
282	992	797	552	219	56	0			
288	1003	810	503	209	48	5			
294	975	797	507	222	46	0			
300	994	790	546	247	41	0			
306	1031	848	574	194	61	0			
312	1026	861	548	237	63	18			
318	1001	814	576	256	69	0			
324	986	895	586	282	54	0			
330	958	831	601	271	84	26			
336	968	885	612	314	95	0			
342	975	848	556	303	86	28			
348	998	868	584	314	116	18			
354	1009	874	589	318	116	13			
360	983	910	593	337	101	9			
366	1005	861	614	342	125	3			
372	996	872	649	335	118	9			
378	936	842	621	355	129	24			
384	1003	831	616	365	146	37			
390	994	865	631	359	153	22			
396	1029	810	679	348	138	13			
402	998	880	666	357	157	35			
408	986	904	685	430	179	20			
414	973	930	653	400	157	39			
420	1022	891	685	421	149	43			
426	996	843	711	382	179	52			
432	979	919	662	417	176	24			
438	938	893	715	451	183	48			
444	983	902	657	432	206	48			
450	1022	887	644	470	191	48			
456	975	936	750	430	213	52			
462	1022	938	732	473	222	73			
468	996	883	713	443	215	41			
474	958	898	747	430	222	65			
480	971	838	713	509	243	58			
486	1005	906	765	507	241	69			
492	1009	891	713	496	245	67			
498	979	943	734	479	245	101			
504	1044		687	498	262	88	9		
510	1001		730	507	243	93	28		
516	1009		713	492	292	112	39		
522	986		786	509	264	108	7		
528	973		780	528	267	110	35		
534	1024		741	520	294	97	28		
540	1044		795	541	310	112	13		
546	988		799	541	290	106	26		
552	1007		773	550	312	129	37		
558	1009		765	558	342	138	20		
564	1037		810	558	322	127	20		
570	1050		777	595	335	131	61		
576	958		801	556	350	176	52		
582	1009		777	569	357	149	22		
588	1024		777	567	372	153	41		
594	981		825	576	365	159	69		
600	1022		829	569	335	161	67		
606	1020		818	591	348	157	30		
612	951		799	567	346	155	63		
618	1016		816	640	382	185	35		
624	986		818	601	348	209	69		
630	971		818	608	402	204	46		
636	979		831	610	398	198	61		
642	1067		795	619	395	213	65		
648	1026		807	629	445	191	88		
654	977		872	659	406	198	67		
660	1046		840	614	415	232	69		
666	1005		831	595	428	215	91		
672	1041		855	657	430	230	95		
678	1035		838	687	430	209	71		
684	998		814	662	466	252	76		
690	992		829	698	440	230	112		
696	1020		848	662	443	252	121		
702	971		891	711	468	262	91		
708	953		878	674	477	264	114		
714	1005		829	687	451	279	121		

TABULATION OF 1000C/CO AS A FUNCTION OF TIME AND BED LENGTH

EXPERIMENT NUMBER 2 A

EXPERIMENTAL CONDITIONS

MOLECULAR SIEVE TYPE 5A, 1/8 INCH DIAMETER CYLINDERS
PRESSURE, 12.50 ATMOSPHERES ABSOLUTE
TEMPERATURE, 0.8 DEGREES CELSIUS
AIR FLOW RATE, 7.50 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 492 PARTS PER MILLION OF CO2

SAMPLE POINT NO.	0	1	2	3	4	5	6	7	8
TIME OF SAMPLE	T	T+1	T+2	T+3	T+4	T+5	T+1	T+2	T+3
ELAPSED TIME (T) IN MINUTES									
0	1007	7	7	0	0	0			
6	1003	25	0	0	7	5			
12	1034	45	0	3	8	0			
18	1045	85	7	5	8	0			
24	956	111	0	0	0	10			
30	1010	160	1	0	0	1			
36	981	193	16	0	1	18			
42	974	204	0	5	1	0			
48	1018	237	14	3	1	0			
54	1016	283	10	7	0	0			
60	1005	303	7	0	3	3			
66	1007	303	0	8	0	0			
72	974	345	8	5	0	0			
78	1012	392	14	0	0	0			
84	1080	423	10	0	0	0			
90	1016	460	34	7	0	3			
96	990	453	30	0	0	0			
102	981	484	36	0	5	0			
108	1014	506	41	0	0	1			
114	1032	530	58	1	8	0			
120	1036	557	56	0	5	5			
126	1021	570	82	8	0	5			
132	957	594	89	12	10	0			
138	976	572	111	0	0	8			
144	945	561	122	0	0	0			
150	970	608	102	7	1	0			
156	972	650	113	1	5	0			
162	1049	645	153	18	5	3			
168	1025	612	142	12	3	0			
174	965	659	169	0	0	5			
180	1036	630	169	10	0	7			
186	1040	701	191	12	0	0			
192	970	659	197	10	8	0			
198	972	698	213	1	0	0			
204	1034	754	235	16	0	1			
210	963	707	246	23	5	0			
216	1031	700	242	10	0	16			
222	987	716	242	29	0	0			
228	999	756	275	41	0	0			
234	999	732	286	36	5	0			
240	992	751	299	32	0	3			
246	1009	762	319	49	3	10			
252	1018	796	349	43	0	0			
258	998	760	328	50	0	10			
264	990	795	332	50	16	1			
270	1016	824	400	58	5	1			
276	970	817	374	65	7	0			
282	1020	829	391	67	3	3			
288	1049	807	422	65	7	0			
294	992	798	380	94	14	0			
300	976	851	427	100	0	5			
306	999	864	440	98	0	10			
312	996	817	442	105	14	0			
318	999	826	455	98	12	0			
324	965	873	509	105	0	0			
330	968	868	480	116	3	7			
336	970	870	508	124	0	3			
342	1003	864	497	138	14	0			
348	979	846	526	160	5	0			
354	931	904	555	149	7	3			
360	1012	886	568	160	18	1			
366	1021	877	546	177	10	8			
372	1007	914	559	186	8	1			
378	988	899	608	180	27	1			
384	950	895	588	186	25	8			
390	1005	888	599	219	32	3			
396	988	965	632	200	21	1			
402	990	903	628	213	52	0			
408	1038	959	623	233	36	3			
414	1005	901	659	250	29	0			
420	988	956	632	253	29	3			
426	1005	968	610	266	36	8			
432	992	924	650	286	69	0			
438	1005	919	672	274	49	3			
444	999	946	716	299	61	7			
450	1007	921	732	303	58	5			
456	961	952	694	316	54	0			
462	1040	946	711	332	69	0			
468	1063	935	711	349	83	14			
474	1009	968	749	369	71	0			
480	1021	939	749	383	80	0			
486	948	935	751	385	87	10			
492	1001	983	771	383	96	0			
498	1007	945	782	422	96	14			
504	1036	961	773	420	96	14			
510	1025	985	778	391	103	21			
516	978	1027	802	403	125	21			
522	981	923	815	458	111	16			
528	946	965	813	414	133	18			
534	1018	994	844	464	127	23			
540	994	1021	848	508	135	21			
546	1025	1020	815	482	158	30			
552	978	981	780	506	157	27			
558	1001	994	817	497	173	27			
564	990	998	855	530	162	21			
570	967	974	848	539	191	43			
576	990	988	831	526	200	19			
582	961	976	870	531	186	32			
588	992		903	550	221	32	0		
594	990		866	548	186	41	3		
600	1020		895	546	226	54	7		
606	1001		877	536	213	38	7		
612	1020		873	590	237	38	1		
618	1023		915	603	259	47	10		
624	967		950	610	272	60	5		
630	965		923	595	250	49	8		
636	1001		829	641	268	43	0		
642	992		923	630	275	54	7		
648	983		866	634	268	65	10		
654	992		888	626	299	67	19		
660	981		895	701	297	65	21		
666	1021		914	689	328	61	23		
672	979		965	665	323	89	7		
678	1007		965	714	327	91	18		
684	988		912	742	325	78	16		
690	959		910	732	354	98	8		
696	999		950	681	378	89	18		
702	981		956	723	358	103	14		
708	972		937	720	394	102	8		
714	974		941	758	398	116	32		

TABULATION OF 1000C/CO AS A FUNCTION OF TIME AND BED LENGTH

EXPERIMENT NUMBER 3 A

EXPERIMENTAL CONDITIONS

MOLECULAR SIEVE TYPE 5A, 1/8 INCH DIAMETER CYLINDERS
PRESSURE, 6.25 ATMOSPHERES ABSOLUTE
TEMPERATURE, -2.1 DEGREES CELSIUS
AIR FLOW RATE, 3.75 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 998 PARTS PER MILLION OF CO2

SAMPLE POINT NO.	0	1	2	3	4	5	6	7	8
TIME OF SAMPLE	T	T+1	T+2	T+3	T+4	T+5	T+1	T+2	T+3
ELAPSED TIME (T) IN MINUTES									
0	1009	3	0	2	0	5			
6	968	14	5	0	2	0			
12	1007	33	0	5	0	0			
18	1007	50	0	0	0	0			
24	1013	65	0	0	3	0			
30	997	92	0	0	0	0			
36	1024	100	3	0	2	0			
42	1026	123	5	0	0	0			
48	977	140	0	5	0	3			
54	1022	171	0	0	0	0			
60	1001	182	0	0	3	0			
66	997	209	3	0	3	2			
72	993	232	7	0	0	0			
78	992	245	6	0	0	0			
84	1008	265	6	0	3	2			
90	978	294	10	0	0	0			
96	979	305	5	5	0	0			
102	1009	328	10	0	0	0			
108	1023	342	13	3	2	0			
114	989	361	14	2	2	0			
120	979	395	15	3	3	2			
126	982	399	21	0	2	0			
132	992	425	20	2	2	6			
138	1020	454	29	0	0	5			
144	1009	484	24	3	0	5			
150	1000	478	35	0	0	3			
156	1017	506	37	0	2	2			
162	1002	544	41	0	0	0			
168	964	555	51	2	0	0			
174	989	575	50	5	2	2			
180	1024	608	62	5	2	2			
186	1020	624	62	3	0	2			
192	1023	627	71	6	0	0			
198	1011	639	73	6	0	0			
204	987	698	85	3	0	2			
210	1002	694	96	0	2	0			
216	1017	697	97	3	2	0			
222	978	731	107	0	2	2			
228	1004	753	122	6	0	5			
234	997	768	137	3	0	2			
240	996	788	146	9	2	3			
246	990	810	148	5	0	0			
252	994	824	157	6	5	0			
258	974	850	171	9	3	0			
264	1000	844	186	6	5	0			
270	981	858	202	0	6	0			
276	979	877	217	13	0	0			
282	1028	893	230	9	3	2			
288	979	892	242	15	2	0			
294	971	921	267	11	0	2			
300	985	944	279	13	0	0			
306	981	944	284	17	2	0			
312	994	936	317	18	0	3			
318	981	964	314	18	2	0			
324	993	966	342	21	0	0			
330	1016	968	358	22	0	0			
336	996	970	389	25	0	2			
342	1001	985	413	26	0	0			
348	989	993	418	36	0	0			
354	1019	990	440	40	0	5			
360	992	971	465	40	0	0			
366	990	1005	489	40	0	0			
372	992	1013	519	50	0	0			
378	989	992	531	55	0	0			
384	1013	959	552	60	6	0			
390	1009	971	582	59	2	0			
396	982	1028	600	69	0	0			
402	1002	990	615	77	3	0			
408	1007	1016	630	81	2	5			
414	1005	1000	669	97	5	2			
420	1004	994	676	95	6	0			
426	992	987	694	106	2	2			
432	986	1009	747	119	2	0			
438	977	1001	734	127	7	0			
444	1026	997	754	127	6	0			
450	1011	1017	781	143	6	0			
456	978	963	783	155	9	0			
462	1020	970	809	162	2	2			
468	1019	987	799	183	6	0			
474	1002	1002	824	193	5	0			
480	1028	1017	836	209	9	3			
486	994	996	855	217	10	2			
492	994	987	877	233	14	0			
498	970	968	899	242	14	0			
504	1035	986	931	256	11	0			
510	997	1007	899	267	14	0			
516	997	998	915	287	18	2			
522	983	1019	931	320	20	2			
528	994	972	934	338	21	0			
534	1003	997	989	340	24	2			
540	1013	1011	974	362	28	3			
546	990	1008	952	387	32	5			
552	982	1012	966	402	30	0			
558	1028	1000	959	417	30	2			
564	981	972	982	445	40	2			
570	1024	1038	989	480	40	3			
576	996	1022	979	484	50	3			
582	992	964	964	515	54	0			
588	1007	971	992	530	58	6			
594	981	1016	968	566	69	0			
600	996	985	1022	559	70	5			
606	1005	1002	1013	587	73	0			
612	989	1017	998	615	75	0			
618	1019	1028	977	649	89	2			
624	984	997	1004	668	95	0			
630	1004	1028	993	667	99	0			
636	1012	1016	997	710	108	5			
642	982	985	1000	714	112	0			
648	993	987	990	735	122	2			
654	1001	971	992	743	140	5			
660	1012	1024	972	762	146	9			
666	974	1005	1000	791	162	7			
672	1030	1008	1000	780	167	7			
678	986	1022	946	822	181	11			
684	1017	1028	1002	843	202	14			
690	1016	1001	1037	867	213	5			
696	1019	998	996	880	212	11			
702	1008	1005	990	900	241	13			
708	1005	1016	987	860	260	18			
714	996	1016	1008	910	273	15			

END OUTPUT 3 BLOCKS

TABULATION OF 1000C/CO AS A FUNCTION OF TIME AND BED LENGTH

EXPERIMENT NUMBER 4 A

EXPERIMENTAL CONDITIONS

MOLECULAR SIEVE TYPE 5A, 1/16 INCH DIAMETER CYLINDERS
PRESSURE, 25.00 ATMOSPHERES ABSOLUTE
TEMPERATURE, 1.2 DEGREES CELSIUS
AIR FLOW RATE, 15.00 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 245 PARTS PER MILLION OF CO2

SAMPLE POINT NO.	0	1	2	3	4	5	6	7	8
TIME OF SAMPLE	T	T+1	T+2	T+3	T+4	T+5	T+1	T+2	T+3
ELAPSED TIME (T) IN MINUTES									
0	1021	6	0	0	0	0			
6	1028	19	0	0	0	2			
12	991	41	2	13	8	0			
18	967	80	0	0	0	0			
24	1032	91	2	13	0	2			
30	1021	119	6	0	21	0			
36	1013	128	0	0	15	4			
42	1028	185	3	24	0	0			
48	1056	178	10	0	2	8			
54	1010	198	4	0	8	0			
60	969	241	0	10	13	17			
66	1032	307	8	0	4	0			
72	954	307	0	4	0	13			
78	986	326	8	0	2	0			
84	1045	322	21	13	0	6			
90	1028	385	17	0	0	8			
96	986	416	37	0	15	4			
102	980	422	24	4	2	0			
108	1021	472	0	19	2	6			
114	995	509	4	10	0	0			
130	1004	507	34	0	19	17			
126	958	549	34	0	0	2			
132	982	559	34	2	0	0			
138	973	596	76	2	0	0			
144	964	653	41	0	2	26			
150	997	623	63	2	19	10			
156	1030	655	65	0	6	0			
162	978	710	89	13	26	2			
168	1060	755	100	8	4	0			
174	1008	731	98	8	4	17			
180	991	738	122	0	8	0			
186	1030	795	146	0	8	21			
192	1025	819	132	15	2	4			
198	993	764	161	0	0	0			
204	999	834	161	26	0	19			
210	947	819	180	2	0	0			
216	1043	860	233	10	0	0			
222	991	888	235	2	15	2			
228	991	917	252	13	0	0			
234	1028	949	254	28	19	0			
240	975	945	302	26	13	0			
246	971	951	311	17	0	4			
252	1021	982	315	32	21	0			
253	1021	967	374	8	4	0			
264	964	954	403	4	24	0			
270	999	967	422	4	0	4			
276	1036	960	457	26	0	0			
282	995	910	468	30	0	0			
288	973	1006	468	32	0	8			
294	991	1006	511	34	0	2			
300	967	1012	564	43	15	2			
306	980	984	603	65	4	4			
312	978	978	594	67	0	10			
318	1012	973	623	82	4	0			
324	967	993	649	87	10	0			
330	975	1032	686	78	8	0			
336	932	984	697	87	8	8			
342	1002	984	742	108	0	15			
348	1002	988	755	117	13	0			
354	1017	971	779	146	0	0			
360	960	1006	808	152	13	0			
366	1019	975	834	150	0	0			
372	1021	1015	849	172	19	0			
378	1015	999	856	198	8	0			
384	1034	1019	864	230	26	6			
390	954	986	921	248	4	6			
396	964	1004	886	239	15	0			
402	991	971	901	283	15	0			
408	954	1056	943	296	4	0			
414	995	954	934	328	19	10			
420	975	962	975	374	15	0			
426	1019	993	973	370	32	0			
432	1025	1036	1021	420	30	4			
438	947	1002	975	413	19	2			
444	1049	969	1006	481	34	0			
450	980	1023	995	505	37	0			
456	991	1023	991	503	32	0			
462	1002	1002	1021	548	52	10			
468	991	991	986	594	54	6			
474	986	1008	1023	585	67	2			
480	1012	1017	991	660	67	8			
486	1015	978	1015	673	67	8			
492	1008	960	1036	690	98	0			
498	1030	1002	943	705	95	39			
504	980	1025	934	747	106	15			
510	1012	1021	986	745	124	6			
516	971	991	1043	786	154	19			
522	1025	971	978	777	165	0			
528	945	1030	978	864	161	0			
534	984	1006	995	823	174	8			
540	1008	984	1012	840	189	0			
546	978	995	982	886	200	8			
552	1028	1010	1034	890	215	24			
558	1010	1002	999	877	237	24			
564	993	956	1006	910	265	30			
570	1023	1010	993	932	289	26			
576	980	1028	1023	945	359	13			
582	1071	1025	1025	936	326	17			
588	1010	1008	999	945	368	34			
594	993	978	999	949	357	28			
600	991	984	980	980	416	30			
606	1012	997	1049	1002	440	65			
612	960	1015	973	995	485	50			
618	1010	1019	1021	980	498	39			
624	988	1023	943	1019	542	63			
630	997	1045	980	999	599	67			
636	1041	1036	1034	984	603	63			
642	995	1039	1021	999	633	108			
648	995	971	982	1032	644	87			
654	999	1019	995	1012	664	106			
660	1025	993	1002	1008	690	100			
666	947	962	1002	995	745	135			
672	1010	993	986	967	762	130			
678	1049	1056	999	982	777	154			
684	984	982	1030	1032	836	167			
690	1015	1039	1006	1008	827	193			
696	1023	975	1012	1021	829	217			
702	962	986	1004	1006	873	217			
708	956	991	1021	1010	884	237			
714	969	999	988	1002	864	246			

TABULATION OF 1000C/CO AS A FUNCTION OF TIME AND BED LENGTH

EXPERIMENT NUMBER 5 A

EXPERIMENTAL CONDITIONS

MOLECULAR SIEVE TYPE 5A,1/16 INCH DIAMETER CYLINDERS
PRESSURE, 12.50 ATMOSPHERES ABSOLUTE
TEMPERATURE, -0.6 DEGREES CELSIUS
AIR FLOW RATE, 7.50 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 499 PARTS PER MILLION OF CO2

SAMPLE POINT NO.	0	1	2	3	4	5	6	7	8
TIME OF SAMPLE ELAPSED TIME (T) IN MINUTES	T	T+1	T+2	T+3	T+4	T+5	T+1	T+2	T+3
0	1014	9	0	2	0	0			
6	1001	13	2	0	2	2			
12	983	24	4	4	0	2			
18	992	33	4	8	6	0			
24	998	36	0	6	2	0			
30	1003	54	0	0	0	0			
36	985	67	4	4	0	2			
42	996	81	0	0	9	0			
48	987	95	6	0	2	2			
54	1014	106	6	0	0	2			
60	998	128	0	6	0	2			
66	985	144	4	0	2	0			
72	987	167	6	4	0	0			
78	994	185	6	4	0	0			
84	1001	210	4	2	0	0			
90	989	243	6	2	6	4			
96	1009	266	2	0	2	0			
102	983	286	6	0	0	0			
108	996	323	6	0	4	0			
114	987	361	2	2	9	6			
120	994	377	13	0	8	0			
126	1007	418	9	2	0	0			
132	1007	463	6	0	0	0			
138	1001	487	13	0	0	0			
144	982	533	17	0	0	2			
150	1001	578	15	6	0	2			
156	1005	601	15	0	0	0			
162	1018	644	25	0	6	2			
168	989	696	25	0	0	0			
174	989	738	25	0	0	0			
180	1009	777	27	0	4	2			
186	998	831	42	2	0	0			
192	1007	881	42	0	0	4			
198	1007	930	45	0	2	0			
204	998	994	60	0	2	0			
210	982	991	65	4	0	0			
216	982	1010	76	4	0	4			
222	975	1003	94	2	0	4			
228	1012	994	101	2	6	0			
234	1010	1007	122	2	0	0			
240	989	1007	142	0	0	2			
246	1000	983	144	4	0	0			
252	998	1000	178	2	0	6			
258	992	998	194	0	0	4			
264	989	1012	212	8	6	0			
270	1003	992	246	6	0	2			
276	1028	998	269	8	4	0			
282	998	996	304	9	2	4			
288	1023	1007	332	11	0	2			
294	1003	1005	377	9	0	0			
300	998	1001	402	13	0	2			
306	1001	1014	456	9	2	6			
312	989	1014	487	4	2	4			
318	980	1000	515	13	0	0			
324	1010	1007	558	9	0	6			
330	1028	978	601	18	9	2			
336	992	991	625	20	4	4			
342	1000	992	680	22	0	0			
348	991	983	731	24	0	2			
354	1019	1003	801	29	2	0			
360	994	1003	813	34	2	0			
366	1005	1007	869	38	8	0			
372	1001	1001	939	47	2	4			
378	1016	1012	960	56	0	0			
384	1014	1000	1000	60	6	0			
390	1009	1000	1005	78	0	4			
396	1014	1000	1010	86	4	0			
402	1003	989	1001	94	6	4			
408	1003	985	1009	108	0	0			
414	987	992	987	130	4	0			
420	985	994	1001	142	8	0			
426	1014	1010	1014	164	2	0			
432	1018	985	1021	180	2	0			
438	992	1016	991	210	0	0			
444	1005	1010	998	225	6	0			
450	1009	1016	1018	255	4	2			
456	962	1009	980	298	6	0			
462	1010	1018	1010	329	4	0			
468	991	971	1012	363	4	0			
474	991	989	1032	408	9	2			
480	1016	1007	1007	433	13	2			
486	1028	1003	978	461	11	0			
492	1000	1012	1012	510	15	0			
498	1014	1012	1000	553	13	0			
504	1000	992	1000	576	20	4			
510	1005	996	1014	623	15	6			
516	1019	1005	1025	657	22	4			
522	996	1014	998	700	27	4			
528	998	1010	975	740	22	0			
534	989	996	1005	806	31	0			
540	1030	991	998	869	34	6			
546	994	1009	1010	910	49	0			
552	998	1010	1001	978	51	0			
558	987	1007	996	1003	58	2			
564	987	1027	985	1010	76	2			
570	996	1001	1012	996	83	0			
576	992	1003	969	994	97	0			
582	1021	991	1001	1014	113	9			
588	989	1001	994	1014	124	13			
594	975	1003	998	989	137	0			
600	983	1003	989	1010	155	2			
606	996	998	991	994	164	2			
612	1000	1001	1012	1001	194	0			

TABULATION OF 1000C/CO AS A FUNCTION OF TIME AND BED LENGTH

EXPERIMENT NUMBER 6 A

EXPERIMENTAL CONDITIONS

MOLECULAR SIEVE TYPE 5A,1/16 INCH DIAMETER CYLINDERS
PRESSURE, 6.25 ATMOSPHERES ABSOLUTE
TEMPERATURE, -1.5 DEGREES CELSIUS
AIR FLOW RATE, 3.75 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 998 PARTS PER MILLION OF CO2

SAMPLE POINT NO.	0	1	2	3	4	5	6	7	8
TIME OF SAMPLE	T	T+1	T+2	T+3	T+4	T+5	T+1	T+2	T+3
ELAPSED TIME (T) IN MINUTES									
0	1024	2	4	3	6	0			
6	1017	11	0	0	0	0			
12	999	21	0	2	0	0			
18	994	19	0	3	0	0			
24	1003	26	0	0	2	0			
30	1005	30	0	0	0	0			
36	998	44	0	0	0	0			
42	1003	49	2	4	0	0			
48	993	64	0	0	0	0			
54	1020	81	2	3	0	0			
60	991	96	0	4	0	2			
66	1021	112	3	0	0	0			
72	994	129	0	3	0	0			
78	991	146	2	0	2	0			
84	1024	173	9	0	0	0			
90	1007	212	2	0	6	2			
96	1007	238	3	2	2	0			
102	987	263	4	0	0	0			
108	1018	306	9	0	2	0			
114	990	322	2	0	3	3			
120	997	360	2	2	10	2			
126	999	386	9	0	3	0			
132	988	454	4	0	0	2			
138	998	487	10	0	0	0			
144	1010	526	11	0	0	0			
150	980	562	4	2	3	4			
156	971	627	10	0	4	0			
162	1024	679	14	0	0	0			
168	1010	744	14	0	0	2			
174	1002	789	15	0	3	2			
180	999	881	19	3	0	0			
186	1012	1029	23	3	0	0			
192	986	1017	19	3	0	0			
198	1010	948	32	0	6	0			
204	973	1002	36	0	0	0			
210	1005	1020	45	0	2	0			
216	983	980	60	2	0	0			
222	980	990	62	2	0	2			
228	988	983	77	3	2	0			
234	1002	982	96	3	0	0			
240	990	965	100	3	2	0			
246	1007	990	101	6	0	0			
252	982	1012	134	4	2	4			
258	995	995	158	4	0	0			
264	1014	976	175	0	0	2			
270	988	967	198	4	0	0			
276	1001	994	236	0	0	0			
282	982	1021	276	3	0	0			
288	984	991	293	2	2	0			
294	994	965	329	4	0	0			
300	990	1003	356	10	0	2			
306	1028	994	401	10	0	3			
312	1010	1010	439	9	0	0			
318	1001	1017	491	9	0	0			
324	982	1028	529	6	0	0			
330	971	1001	558	11	6	0			
336	983	1010	641	11	2	2			
342	999	1001	672	18	0	0			
348	998	1025	717	13	0	2			
354	1001	1014	776	13	0	0			
360	973	1009	863	21	0	0			
366	994	1013	938	19	0	4			
372	971	1021	1001	24	0	0			
378	1010	1017	997	28	3	0			
384	993	1016	999	30	4	0			
390	1005	1013	1002	49	3	0			
396	997	984	999	54	6	3			
402	976	1024	998	69	3	0			
408	1018	994	986	78	0	0			
414	1007	971	1002	85	0	0			
420	976	983	994	104	2	0			
426	988	1017	1007	107	4	2			
432	987	987	1052	133	3	0			
438	979	1051	1002	154	2	0			
444	978	991	1025	172	7	0			
450	1022	1014	1014	216	3	0			
456	963	975	1012	244	6	0			
462	1012	987	991	261	3	0			
468	1012	982	1003	303	11	2			
474	1010	1020	975	334	7	0			
480	1001	1001	991	372	9	6			
486	1020	1007	1012	419	9	2			
492	994	1021	1012	449	9	0			
498	982	1017	1007	461	11	2			
504	1002		1013	523	9	3	0		
510	1036		1012	570	9	6	0		
516	1010		988	626	15	0	0		
522	1010		1003	685	13	0	2		
528	1001		1012	732	10	0	0		
534	1020		1013	814	14	0	0		
540	999		1005	878	18	6	0		
546	1022		1013	958	22	3	6		
552	1002		993	994	30	3	0		
558	994		976	1036	30	2	0		
564	998		960	986	39	2	0		
570	983		1024	1017	43	6	3		
576	980		995	1010	58	4	0		
582	1017		990	1025	67	0	0		
588	1002		987	999	69	6	0		
594	980		965	990	86	0	0		
600	1009		993	999	101	0	7		
606	1014		1014	1009	114	4	0		
612	950		991	999	130	0	0		

END OUTPUT 2 BLOCKS

TABULATION OF 1000C/CO AS A FUNCTION OF TIME AND BED LENGTH

EXPERIMENT NUMBER 1 B

EXPERIMENTAL CONDITIONS

MOLECULAR SIEVE TYPE 5A, 1/16 INCH DIAMETER CYLINDERS
PRESSURE, 6.25 ATMOSPHERES ABSOLUTE
TEMPERATURE, 0.7 DEGREES CELSIUS
AIR FLOW RATE, 3.75 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 996 PARTS PER MILLION OF CO2

SAMPLE POINT NO.	0	1	2	3	4	5	6	7	8
TIME OF SAMPLE	T	T+1	T+2	T+3	T+4	T+5	T+1	T+2	T+3
ELAPSED TIME (T) IN MINUTES									
0	1000	4	3	6	0	3			
6	1000	11	4	0	0	0			
12	967	11	0	0	0	0			
18	1017	18	0	2	0	0			
24	994	26	0	0	2	0			
30	981	34	0	0	0	0			
36	1009	44	0	0	0	0			
42	993	47	0	0	2	0			
48	994	64	2	3	0	0			
54	1005	77	0	2	2	0			
60	978	92	2	4	0	3			
66	994	100	3	0	3	0			
72	1000	122	3	2	0	0			
78	992	139	4	3	0	0			
84	1016	178	6	2	0	0			
90	990	206	2	4	4	0			
96	1034	239	3	0	0	0			
102	998	261	3	0	0	0			
108	1019	300	3	0	0	0			
114	1005	336	0	0	2	0			
120	992	359	8	0	6	2			
126	982	400	0	0	0	0			
132	987	446	8	2	0	0			
138	996	472	8	0	0	0			
144	982	532	10	0	0	2			
150	996	562	10	4	2	0			
156	1017	637	7	0	0	0			
162	1017	677	13	0	0	0			
168	1026	717	18	2	0	0			
174	1005	795	18	3	0	2			
180	998	867	17	0	0	0			
186	998	974	23	0	3	0			
192	1008	985	22	2	0	3			
198	982	1004	34	0	0	0			
204	994	1004	33	2	0	0			
210	1012	992	40	0	0	3			
216	987	979	55	0	0	2			
222	979	1007	59	0	0	2			
228	1015	1002	68	3	0	0			
234	989	997	83	3	0	3			
240	1005	1002	97	0	2	0			
246	1005	987	101	7	0	0			
252	998	1000	134	4	2	0			
258	1017	1004	152	0	0	2			
264	990	1016	164	0	2	0			
270	986	992	197	3	0	3			
276	1001	983	225	2	0	0			
282	983	1008	261	3	3	0			
288	1004	992	291	4	0	4			
294	986	986	323	11	3	0			
300	989	1011	351	11	0	2			
306	979	1000	393	7	3	6			
312	1011	996	431	10	2	0			
318	971	985	482	7	0	0			
324	998	1028	503	4	3	0			
330	986	970	551	8	0	2			
336	986	1011	612	14	0	3			
342	1000	986	672	15	0	0			
348	981	972	742	13	0	2			
354	987	992	777	14	0	0			
360	977	1007	859	17	0	0			
366	1001	972	930	18	0	2			
372	1000	1011	990	26	0	6			
378	997	1000	993	29	2	0			
384	979	994	1016	33	4	0			
390	982	1004	992	48	0	3			
396	1005	1005	1015	44	4	0			
402	970	1016	1011	56	3	0			
408	1016	1015	993	62	0	0			
414	989	986	1005	86	0	0			
420	983	1002	985	93	0	2			
426	1000	1030	1022	107	6	6			
432	1012	968	1030	124	2	0			
438	977	996	1007	146	3	0			
444	986	978	989	163	4	0			
450	1013	992	1023	193	2	2			
456	979	998	986	220	2	2			
462	998	1012	1009	257	2	0			
468	986	998	994	283	6	2			
474	996	990	982	315	4	0			
480	1017		993	355	7	2	0		
486	990		1001	394	11	0	3		
492	1000		985	439	10	0	0		
498	1000		1020	471	10	0	3		
504	1005		1020	503	11	2	0		
510	1002		1000	552	8	0	3		
516	1028		1000	614	14	0	3		
522	998		1009	657	7	0	0		
528	1004		1000	720	13	2	0		
534	1005		986	783	13	3	0		
540	1012		1000	869	15	6	0		
546	997		1019	937	17	2	0		
552	989		1026	998	19	0	0		
558	1000		983	1017	26	0	3		
564	1009		972	1009	36	2	3		
570	987		1031	983	41	4	3		
576	981		1002	982	52	0	2		
582	1030		1020	1005	62	0	0		
588	990		1012	1031	68	6	0		
594	979		989	990	81	0	0		
600	978		996	1015	90	0	2		
606	978		1007	1008	98	3	2		
612	994		1009	1016	123	2	0		

TABULATION OF 1000C/CO AS A FUNCTION OF TIME AND BED LENGTH

EXPERIMENT NUMBER 2 B

EXPERIMENTAL CONDITIONS

MOLECULAR SIEVE TYPE 5A,1/16 INCH DIAMETER CYLINDERS
PRESSURE, 6.25 ATMOSPHERES ABSOLUTE
TEMPERATURE, 1.7 DEGREES CELSIUS
AIR FLOW RATE, 3.75 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 999 PARTS PER MILLION OF CO2

SAMPLE POINT NO.	0	1	2	3	4	5	6	7	8
TIME OF SAMPLE	T	T+1	T+2	T+3	T+4	T+5	T+1	T+2	T+3
ELAPSED TIME (T) IN MINUTES									
0	997	6	2	1	0	1			
6	1001	12	0	0	0	0			
12	989	17	5	1	2	1			
18	1019	21	0	0	0	2			
24	1027	33	0	0	0	0			
30	988	36	0	1	4	4			
36	1015	50	0	0	0	0			
42	1023	52	1	4	0	0			
48	1027	66	0	0	0	0			
54	982	71	1	1	6	0			
60	1020	94	2	2	0	0			
66	1008	102	0	2	0	1			
72	986	130	2	0	2	0			
78	1028	147	1	0	1	0			
84	1015	177	5	0	2	1			
90	1015	216	4	0	2	0			
96	980	250	5	0	0	1			
102	981	261	0	2	0	4			
108	1004	318	9	0	2	0			
114	991	337	8	5	4	0			
120	982	384	4	0	5	2			
126	982	414	10	0	0	1			
132	957	464	8	2	1	0			
138	1008	494	10	0	4	0			
144	1026	555	10	2	5	0			
150	966	582	6	0	5	0			
156	969	654	12	0	4	1			
162	1008	668	18	0	0	0			
168	993	727	16	0	0	2			
174	982	789	17	1	1	5			
180	1009	873	25	1	0	0			
186	999	972	24	0	1	0			
192	1001	1001	27	1	2	0			
198	989	1007	41	0	0	0			
204	1003	1011	32	2	2	0			
210	993	992	56	0	0	8			
216	1038	980	52	0	0	2			
222	980	1000	73	0	0	1			
228	973	1022	75	4	1	1			
234	1011	1001	94	4	2	1			
240	1015	984	101	0	1	0			
246	1009	1018	119	2	0	1			
252	1014	985	136	1	6	0			
258	1000	1015	151	4	1	0			
264	1046	989	181	6	1	1			
270	984	991	204	5	5	0			
276	1031	1037	248	2	1	0			
282	996	1001	267	8	0	1			
288	992	1009	323	9	6	0			
294	1016	1031	340	2	0	4			
300	1005	962	378	2	2	1			
306	1012	991	398	10	0	5			
312	992	993	470	4	0	4			
318	1014	1000	492	10	1	0			
324	1031	970	549	12	0	0			
330	1023	1005	595	16	0	0			
336	993	1018	635	17	0	1			
342	982	1050	703	13	0	2			
348	1009	982	734	16	5	0			
354	1019	977	817	23	0	0			
360	989	1022	892	24	0	1			
366	1000	991	939	31	0	5			
372	997	1037	969	29	0	0			
378	1022	981	973	32	9	4			
384	1031	982	1003	48	2	0			
390	1000	1020	1014	46	0	8			
396	988	1015	992	65	0	5			
402	1015	1019	985	69	0	0			
408	988	1000	1003	86	1	4			
414	989	991	1037	88	0	0			
420	999	980	1031	116	1	0			
426	996	1011	997	120	0	2			
432	973	1005	991	143	2	1			
438	999	972	1028	155	0	0			
444	1003	982	982	180	5	5			
450	1001	995	1018	208	2	2			
456	1016	1012	981	230	9	0			
462	980	976	1000	305	1	0			
468	996	1007	996	336	4	1			
474	1019	1000	993	364	3	6			
480	993		1014	382	8	0	4		
486	969		993	409	8	5	0		
492	1026		1026	462	8	2	2		
498	984		970	493	13	0	4		
504	1056		985	539	12	1	2		
510	1014		1009	593	10	4	6		
516	1012		974	641	12	2	0		
522	1014		969	703	10	2	1		
528	970		1001	757	14	4	4		
534	1022		982	855	18	5	2		
540	961		1008	868	23	0	0		
546	978		1015	942	25	0	4		
552	1014		957	1014	31	0	4		
558	1026		977	997	28	4	1		
564	1000		1015	1031	43	2	1		
570	986		996	1028	54	1	4		
576	978		1004	1009	71	2	1		
582	991		1014	978	69	2	0		
588	984		1012	1003	88	5	0		
594	1020		1028	1012	96	5	0		
600	1014		993	997	107	2	0		
606	1030		1014	991	128	0	1		
612	978		1005	1003	151	9	0		
618	1003		961	988	155	10	0		
624	1019		1000	962	199	9	0		
630	978		1001	993	226	2	1		
636	1008		996	1015	249	6	0		
642	1001		1024	985	286	13	1		
648	1016		957	978	314	5	4		
654	1011		1023	1001	356	9	0		
660	986		992	978	394	2	0		
666	1001		1007	992	424	5	4		
672	989		1009	969	460	12	0		
678	982		997	1003	493	17	0		
684	1012		978	1018	542	20	1		
690	974		984	1003	569	18	0		
696	967		1011	981	637	24	1		
702	995		1014	1023	681	20	5		
708	977		1004	997	742	31	1		
714	991		1030	989	814	32	4		

TABULATION OF 1000C/CO AS A FUNCTION OF TIME AND BED LENGTH

EXPERIMENT NUMBER 3 B

EXPERIMENTAL CONDITIONS

MOLECULAR SIEVE TYPE 5A,1/16 INCH DIAMETER CYLINDERS
PRESSURE, 6.25 ATMOSPHERES ABSOLUTE
TEMPERATURE, -0.3 DEGREES CELSIUS
AIR FLOW RATE, 5.00 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 1010 PARTS PER MILLION OF CO_2

SAMPLE POINT NO.	0	1	2	3	4	5	6	7	8
TIME OF SAMPLE	T	T+1	T+2	T+3	T+4	T+5	T+1	T+2	T+3
ELAPSED TIME (T) IN MINUTES									
0	994	8	0	4	0	1			
6	1022	35	1	0	0	0			
12	1040	48	0	0	0	0			
18	969	71	3	0	0	0			
24	958	113	0	1	1	0			
30	1028	127	3	4	0	0			
36	986	158	0	0	0	0			
42	1020	178	0	4	0	0			
48	1017	213	11	0	0	4			
54	1013	242	9	0	4	4			
60	972	277	16	0	5	3			
66	1021	307	12	0	0	0			
72	985	355	12	0	0	0			
78	967	391	8	1	0	0			
84	994	400	24	4	8	0			
90	1028	466	14	7	0	3			
96	1001	505	15	0	4	1			
102	989	565	27	0	4	3			
108	1008	621	39	0	5	0			
114	984	665	39	0	0	1			
120	982	700	38	0	3	1			
126	994	811	48	0	0	0			
132	1000	844	63	5	0	0			
138	969	927	67	0	0	3			
144	1001	976	83	4	3	0			
150	989	1012	83	0	0	3			
156	997	1048	106	0	0	3			
162	1018	989	134	0	0	5			
168	1018	997	149	4	0	3			
174	1034	974	178	5	1	0			
180	997	993	187	9	3	1			
186	1005	1009	218	7	0	0			
192	998	980	245	7	0	0			
198	1001	988	294	14	9	0			
204	994	989	311	8	0	0			
210	1029	1037	348	14	1	0			
216	1028	988	408	26	0	0			
222	1008	965	450	22	1	0			
228	1036	1023	478	19	1	0			
234	946	973	521	24	1	4			
240	963	986	545	27	0	0			
246	962	980	590	46	0	1			
252	977	1006	660	31	1	4			
258	1033	996	772	44	0	0			
264	1020	1029	748	58	0	0			
270	996	994	828	71	0	0			
276	1004	984	935	74	0	0			
282	1020	977	998	87	1	0			
288	967	1010	994	114	1	0			
294	989	1004	967	129	1	1			
300	982	1025	1012	153	14	0			
306	997	956	986	169	11	0			
312	1017	997	1009	177	12	0			
318	1005	1021	1052	217	4	0			
324	1018	981	986	244	9	0			
330	1018	1024	986	273	11	0			
336	982	998	972	308	15	0			
342	1001	1004	969	351	12	0			
348	990	981	965	400	7	0			
354	1023	980	976	430	24	4			
360	1053	988	974	467	19	0			
366	969	993	984	497	20	0			
372	994	1004	1029	567	32	0			
378	1021	1021	1006	592	36	0			
384	976	1052	1001	654	36	0			
390	989	997	974	757	48	0			
396	1020	1012	955	831	51	0			
402	967	974	967	886	60	5			
408	1024	1005	955	962	67	3			
414	1025	977	1012	961	83	3			
420	984	1026	1030	984	84	0			
426	994	997	985	1046	99	1			
432	1008	1012	1018	1021	125	11			
438	981	990	1016	1021	147	9			
444	969	993	1002	978	175	14			
450	967	1001	1002	1029	186	11			
456	965	961	990	984	226	5			
462	984	988	993	990	256	9			
468	989	997	1002	976	296	11			
474	1041	1034	1002	1024	324	16			
480	1005		990	970	375	16	1		
486	993		1052	1004	388	18	0		
492	943		986	978	423	22	0		
498	1001		1004	993	470	16	0		
504	1012		1018	1020	506	31	0		
510	1026		966	1024	535	31	0		
516	1002		972	1038	650	43	0		
522	1025		1021	989	668	38	5		
528	1009		1006	963	753	48	0		
534	992		1012	954	761	71	5		
540	951		1013	1020	879	74	0		
546	988		996	993	962	82	0		
552	989		997	1008	1006	92	0		
558	986		1025	1026	1004	99	3		
564	966		953	1022	981	129	1		
570	1009		973	997	1013	143	12		
576	972		1013	1002	1004	169	22		
582	1018		1028	1028	1009	183	19		
588	972		1029	1044	1014	222	22		
594	966		1009	984	962	244	27		

TABULATION OF 1000C/CO AS A FUNCTION OF TIME AND BED LENGTH

EXPERIMENT NUMBER 4 B

EXPERIMENTAL CONDITIONS

MOLECULAR SIEVE TYPE 5A,1/16 INCH DIAMETER CYLINDERS
PRESSURE, 6.25 ATMOSPHERES ABSOLUTE
TEMPERATURE, -2.3 DEGREES CELSIUS
AIR FLOW RATE, 7.50 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 1004 PARTS PER MILLION OF CO2

SAMPLE POINT NO.	0	1	2	3	4	5	6	7	8
TIME OF SAMPLE ELAPSED TIME (T) IN MINUTES	T	T+1	T+2	T+3	T+4	T+5	T+1	T+2	T+3
0	1006	116	6	0	1	0			
6	1026	186	8	0	1	0			
12	1010	238	17	1	2	1			
18	1025	285	20	2	1	0			
24	993	320	22	1	0	5			
30	997	370	33	0	1	0			
36	1014	413	44	5	0	4			
42	1017	459	51	6	0	0			
48	1011	518	69	8	0	0			
54	1011	555	76	9	0	0			
60	1010	593	85	10	2	2			
66	1005	641	107	12	0	0			
72	995	689	124	12	5	0			
78	1033	745	138	12	2	0			
84	1018	836	171	17	0	0			
90	1002	993	202	10	4	0			
96	985	1007	234	18	0	0			
102	1001	1010	250	25	0	0			
108	981	1001	279	28	4	0			
114	1001	1007	322	36	5	0			
120	1010	1014	368	40	6	0			
126	1021	1005	388	49	6	1			
132	1010	1006	437	59	10	0			
138	978	997	484	71	6	2			
144	990	994	520	83	9	0			
150	1003	990	560	93	10	1			
156	1009	997	617	112	12	0			
162	995	1001	675	123	10	2			
168	1013	999	722	144	16	1			
174	973	986	807	172	18	4			
180	998	994	924	196	14	2			
186	994	1021	1019	238	17	4			
192	1003	1001	995	270	24	8			
198	991	994	997	291	29	1			
204	1023		1009	329	33	6	0		
210	986		995	360	47	5	0		
216	1005		1001	393	51	8	1		
222	989		983	436	55	8	4		
228	978		1013	491	71	5	0		
234	995		986	527	89	9	0		
240	977	990	579	99	14	0			
246	1001	993	635	115	14	0			
252	986	1011	697	131	16	1			
258	986	991	754	147	14	2			
264	994	993	793	172	16	0			
270	994	1006	866	200	18	6			
276	990	1007	927	234	24	4			
282	1011	1005	987	262	24	6			
288	1022	1045	999	298	31	2			
294	986		981	336	37	4	0		
300	974		993	352	43	5	1		
306	987		1011	393	52	4	2		
312	999		1002	433	57	5	0		
318	1005		999	480	72	6	4		
324	998		1009	534	75	14	5		
330	1007		975	571	99	16	1		
336	990		1010	627	112	14	6		
342	1001		991	675	134	12	0		
348	991		1011	720	150	16	1		
354	1006		994	801	172	17	2		
360	1006		998	876	194	20	8		
366	1013			935	231	24	2	2	
372	1005			1010	259	24	1	2	
378	989			1006	294	31	2	2	
384	987			1003	330	36	5	0	
390	1027			994	356	41	6	4	
396	1006			986	399	51	6	0	
402	973			1002	423	56	10	1	
408	1002			1026	469	71	12	0	
414	1001			982	514	75	14	0	
420	1006			989	560	96	10	2	
426	1018			1003	622	109	8	0	
432	973			1002	669	127	17	8	
438	1010			985	730	140	12	1	
444	974			1013	777	167	22	4	
450	1001			1013	841	191	16	4	
456	989			1003	943	210	21	4	
462	994			991	997	254	29	6	
468	1023			1025	991	291	26	4	
474	1014			997	1001	320	36	4	
480	1003			1017	982	357	47	6	
486	999			1013	1019	386	49	9	
492	995			1011	993	420	64	6	
498	987			1009	1006	464	69	8	
504	997			970	1010	507	88	10	
510	1005			1002	985	566	99	10	
516	991			1010	1005	614	109	10	
522	993			999	1009	670	130	14	
528	982			1007	1023	732	147	14	
534	1011			975	1021	792	170	14	
540	994			1002	1002	870	188	18	
546	1026			993	1014	934	226	18	
552	1009			1019	1003	985	242	25	
558	1009			1006	1002	975	287	28	
564	1002			1007	998	998	309	36	
570	1007			1003	1005	998	361	36	
576	994			1017	994	1005	382	51	
582	1010			981	1001	994	428	59	
588	1011			997	1007	1011	460	68	
594	1015			997	994	991	508	80	
600	1021			1009	1017	1001	575	92	
606	1001			1018	1007	983	606	108	
612	995			998	1014	1023	671	124	
618	999			986	1013	1015	729	140	

TABULATION OF 1000C/CO AS A FUNCTION OF TIME AND BED LENGTH

EXPERIMENT NUMBER 5 B

EXPERIMENTAL CONDITIONS

MOLECULAR SIEVE TYPE 5A,1/16 INCH DIAMETER CYLINDERS
PRESSURE, 6.25 ATMOSPHERES ABSOLUTE
TEMPERATURE, 0.9 DEGREES CELSIUS
AIR FLOW RATE, 7.50 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 501 PARTS PER MILLION OF CO2

SAMPLE POINT NO.	0	1	2	3	4	5	6	7	8
TIME OF SAMPLE ELAPSED TIME (T) IN MINUTES	T	T+1	T+2	T+3	T+4	T+5	T+1	T+2	T+3
0	992	96	2	4	1	1			
6	1001	154	4	4	4	2			
12	1010	195	13	8	0	0			
18	969	239	15	4	6	2			
24	994	264	13	0	1	0			
30	973	306	24	11	0	0			
36	989	342	32	8	4	1			
42	1007	377	27	1	8	0			
48	987	404	36	2	4	0			
54	1010	439	43	2	6	2			
60	982	462	52	2	1	1			
66	994	506	77	11	1	0			
72	961	515	82	0	4	0			
78	1008	550	82	18	8	1			
84	1007	589	98	9	0	4			
90	1015	614	108	11	9	9			
96	989	632	130	8	0	4			
102	998	664	142	8	0	1			
108	999	706	147	11	0	0			
114	1028	734	165	18	1	0			
120	980	741	176	22	8	0			
126	1021	775	202	24	2	1			
132	969	800	213	20	6	0			
138	1013	816	245	25	0	6			
144	998	823	252	43	4	0			
150	994	835	273	32	9	1			
156	998	870	299	43	11	1			
162	982	900	312	39	6	0			
168	1022	943	321	48	9	8			
174	976	923	352	57	2	2			
180	961	954	370	62	6	1			
186	991	934	407	73	13	0			
192	989	994	427	82	15	0			
198	999	989	441	82	11	2			
204	999	1001	483	89	2	0			
210	1008	1031	501	94	15	4			
216	980	1007	536	98	6	6			
222	1022	985	570	119	22	11			
228	1005	1014	577	131	11	0			
234	987	1005	598	142	25	4			
240	966	982	626	147	18	4			
246	980	1005	660	190	22	8			
252	1012	992	683	181	22	0			
258	1003	1014	717	204	27	9			
264	1005		747	207	22	2	0		
270	1012		761	220	29	0	9		
276	1008		812	255	36	8	6		
282	1014		835	262	46	2	2		
288	1003		854	292	39	8	0		
294	985		874	324	50	8	2		
300	976		936	324	54	9	1		
306	991		939	358	50	11	1		
312	1005		985	370	66	13	2		
318	1010		978	404	68	6	1		
324	996		1005	437	80	4	1		
330	980		975	464	85	13	0		
336	975		1035	478	89	16	0		
342	1017		991	513	100	22	0		
348	998		1014	543	117	9	13		
354	1012		994	547	128	13	1		
360	1008		994	586	144	9	8		
366	985		975	607	147	15	1		
372	991		976	619	147	18	8		
378	996			665	174	24	4	0	
384	991			674	181	22	2	1	
390	1030			740	199	25	4	1	
396	971			750	220	29	6	0	
402	999			780	245	27	0	0	
408	971			824	252	41	2	2	
414	994			835	282	34	11	0	
420	1022			872	301	31	9	4	
426	1007			879	308	48	9	9	
432	975			904	324	48	8	4	
438	1010			971	372	66	8	9	
444	1021			991	395	73	8	0	
450	964			982	414	80	6	0	
456	1007			994	432	75	15	15	
462	1022			1017	448	100	8	9	
468	984			1007	487	87	18	1	
474	978			998	499	115	15	0	
480	1008			1012	533	119	8	0	
486	980			987	545	119	15	0	
492	1012			1012	607	138	16	6	
498	1019			984	648	149	13	0	
504	991			1003	656	167	27	0	
510	992			998	678	176	27	0	
516	1019				710	191	29	6	0
522	1003				748	206	31	2	0
528	969				747	223	32	8	0
534	994				764	257	32	6	0
540	1003				784	268	45	11	6
546	978				844	266	38	9	0
552	1038				879	287	36	4	2
558	978				918	317	48	8	4
564	992				908	342	55	2	0
570	984				939	374	66	9	0
576	985				971	388	73	9	0
582	976				1031	434	75	8	6
588	994				984	466	82	2	2
594	992				1019	476	87	11	1
600	994				1019	515	92	8	0
606	1019				1017	511	100	15	1
612	984				1005	542	121	15	2
618	968				985	563	135	15	9
624	973				989	609	142	20	8
630	987				1033	651	151	20	6
636	1014				975	660	170	20	8
642	1026				1005	695	184	24	2
648	975				1003	695	190	27	2
654	991				994	752	220	31	4
660	957				1012	810	220	27	9
666	1022				994	796	237	36	2
672	996				989	819	276	46	13
678	982				1017	847	289	50	11
684	996				998	879	305	52	9
690	1015				1024	906	322	61	8
696	996				1008	915	345	68	2
702	987				976	971	372	59	6
708	1030				994	991	411	77	11
714	999				998	996	423	82	9

TABULATION OF 1000C/CO AS A FUNCTION OF TIME AND BED LENGTH

EXPERIMENT NUMBER 6 B

EXPERIMENTAL CONDITIONS

MOLECULAR SIEVE TYPE 5A,1/16 INCH DIAMETER CYLINDERS
PRESSURE, 6.25 ATMOSPHERES ABSOLUTE
TEMPERATURE, 1.3 DEGREES CELSIUS
AIR FLOW RATE, 7.50 STANDARD CUBIC FEET PER MINUTE
FEED CONCENTRATION, 253 PARTS PER MILLION OF CO2

SAMPLE POINT NO.	0	1	2	3	4	5	6	7	8
TIME OF SAMPLE	T	T+1	T+2	T+3	T+4	T+5	T+1	T+2	T+3
ELAPSED TIME (T) IN MINUTES									
0	986	90	11	3	0	3			
6	1001	145	22	0	0	0			
12	992	187	7	3	3	5			
18	992	223	22	0	9	0			
24	984	251	5	9	7	7			
30	996	283	22	3	0	0			
36	1001	296	24	0	7	0			
42	1030	338	32	0	11	0			
48	1041	357	37	13	0	3			
54	979	387	45	0	0	5			
60	982	419	54	7	0	0			
66	1018	423	64	5	0	0			
72	982	457	62	17	5	0			
78	973	499	68	9	0	0			
84	1003	504	73	5	3	0			
90	979	516	83	11	0	0			
96	1003	561	94	5	0	0			
102	1007	578	107	7	0	0			
108	984	614	126	13	5	0			
114	992	576	147	9	0	11			
120	1007	631	128	13	9	11			
126	1003	642	164	20	3	0			
132	999	667	151	26	0	0			
138	992	695	183	15	0	5			
144	1003	705	194	30	3	0			
150	1024	725	209	30	7	0			
156	1028	771	213	34	0	5			
162	1028	754	240	20	3	15			
168	975	771	232	39	17	9			
174	1032	799	257	26	3	0			
180	1009	810	293	30	15	13			
186	994	812	300	39	7	0			
192	994	839	315	58	0	0			
198	986	852	317	54	15	7			
204	1003	854	334	58	9	3			
210	1020	880	353	66	15	0			
216	1032	888	372	71	0	0			
222	1003	882	402	81	13	11			
228	1016	922	402	85	15	0			
234	990	903	412	94	0	5			
240	999	926	457	94	7	0			
246	994	952	451	115	15	0			
252	996	924	482	109	11	7			
258	1011	973	497	119	11	9			
264	979	975	493	136	24	7			
270	990	969	525	130	24	9			
276	1009	999	553	132	20	0			
282	1013	988	563	151	37	7			
288	973	973	582	185	34	0			
294	992	1013	601	185	34	5			
300	1007	1001	612	200	22	0			
306	1026	982	621	196	39	5			
312	1024	973	642	204	45	5			
318	977	984	688	217	37	3			
324	1011	1003	674	247	34	9			
330	992	988	705	228	51	0			
336	975	1013	708	268	51	20			
342	1001	975	718	283	49	7			
348	994	1005	742	296	66	9			
354	1016	1003	782	306	60	9			
360	1026	1003	780	317	49	9			
366	975	1001	786	334	87	3			
372	1054	1007	837	340	73	15			
378	999	1001	833	347	73	7			
384	1009	1005	854	372	90	15			
390	1007	1009	839	389	117	22			
396	996		890	406	98	11	7		
402	973		886	421	100	13	0		
408	988		905	423	117	13	0		
414	1026		916	465	121	26	0		
420	994		971	480	141	22	9		
426	967		960	497	134	26	15		
432	1001		965	519	134	15	15		
438	988		954	538	151	17	3		
444	960		984	542	175	24	0		
450	1007		975	574	181	24	0		
456	1003		990	563	194	37	0		
462	960		1016	608	194	34	5		
468	1007		990	597	194	37	9		
474	1013		990	652	196	39	0		
480	992		1011	648	209	45	11		
486	984		1005	676	230	41	13		
492	984		984	699	236	54	3		
498	1003		1009	705	260	56	15		
504	994		994	718	281	64	9		
510	1011		986	744	279	64	24		
516	1007		982	761	302	71	17		
522	1007		1001	763	306	62	13		
528	1022			784	327	66	15	0	
534	999			795	340	90	5	0	
540	984			814	353	90	9	7	
546	1005			833	378	92	0	5	
552	1009			833	398	107	3	7	
558	1001			858	406	94	22	13	
564	1005			894	419	94	30	5	
570	969			882	440	119	9	3	
576	982			922	444	128	17	9	
582	992			931	468	130	24	24	
588	965			962	482	145	37	11	
594	988			935	482	149	17	5	
600	977			982	512	155	24	0	
606	1016			954	529	170	37	0	
612	1024			973	555	177	47	0	
618	1013			971	578	198	28	11	
624	1020			990	593	194	49	13	
630	1026			950	595	209	37	0	
636	1020			990	614	189	28	0	
642	954			1026	612	238	39	0	
648	986			994	650	232	49	24	
654	984			982	686	249	51	9	
660	979			990	703	257	60	9	
666	996			1001	701	272	58	3	
672	986			992	714	291	64	5	
678	984			1003	729	298	64	13	
684	986			1024	763	298	83	5	
690	1022				742	327	75	9	3
696	992				784	344	90	20	9
702	1018				803	359	98	20	0
708	1005				822	355	87	22	0
714	1005				854	349	90	11	5

Appendix G

BASIS FOR THE COMPARISON OF VALUES OF E, X_F AND Y_F

A careful examination of the computer programme and the equations upon which it is based reveals some slight differences in the meanings of E, X_F and Y_F. The following table allows one to relate the two sets of values. (α has been made = 2 for ease of comparison.)

	Theory	Programme
X	$-\frac{2}{3}\frac{V_o}{1-V_o}\frac{(R+1)}{R^2}Q\frac{X_F}{E}$	$-\frac{(R+1)}{R^2}Q\frac{X_F}{E}$
Y	$\frac{Y_F}{s^2T}$	$\frac{Y_F}{s^2T}$
Z	$\frac{V_1}{3}\frac{(s+1)}{s^2}R^2\frac{Y_F}{X_F}$	$\frac{(s+1)}{s^2}R^2\frac{Y_F}{X_F}$

It is apparent from the expressions for Y that Y_F has the same meaning in both instances. But from the expressions for Z, one may say that $(X_F)_{Pr} = \frac{3}{V_1}(X_F)_{Th}$. Similarly, from the expressions

for X, $(E)_{Pr} = \frac{2}{2} \frac{1-V_o}{V_o V_1} (E)_{Th}$.

Now if V_2 is defined as the pore volume per unit volume of the bed, V_1 which was defined in Chapter 3, may be rewritten as

$$\frac{1-V_o}{1-V_o-V_2}$$

Therefore $(X_F)_{Pr} = \frac{3(1-V_o-V_2)}{(1-V_o)} (X_F)_{Th}$

and $(E)_{Pr} = \frac{2}{2} (1-V_o-V_2) \frac{(E)_{Th}}{V_o}$

CALCULATIONS BASED UPON PHYSICAL MEASUREMENTS

The operating conditions used in the following calculations have been chosen to correspond to Run 6A.

X_F

Dworjanyn[5E] has measured a pore diffusion coefficient for the self diffusion of CO_2 in a tube packed with 4A crystals. He found that it was related to the corresponding free gas coefficient by a factor of .745. If this is taken as a measure of tortuosity, it agrees fairly well with the simple model which predicts a figure of $1/\sqrt{2}$. Since the "D_p" used in the present work is an effective pellet diffusion coefficient rather

than a pore diffusion coefficient, one must also multiply by $\frac{V_2}{1-V_o}$ to obtain a value for D_p from the gas diffusion coefficient.

The free gas diffusion coefficient for Air-CO_2 may be calculated, from the general formula of Hirschfelder et al [16], to be $\frac{.1292}{P}$. For a pressure of 6.25 ata, $D = .02066$ cm^2/sec. Using Dworjanyn's tortuosity factor, $D_p = \frac{.745\ V_2}{1-V_o}$ .02066 For 1/16" diameter pellets, S = 1/32" = .0795 cm

$\frac{S^2}{D_p}$ is therefore equal to $\frac{.409\ (1-V_o)}{V_2}$

If this is used as $(X_F)_{Th}$, then $(X_F)_{Pr} = \frac{3 \times .409\ (1-V_o-V_2)}{V_2}$

Using Dworjanyn's [5H] values of V_o (.337) and V_2 (.234), $(X_F)_{Pr} = 2.25$.

$\frac{E}{}$

A flow rate of 3.75 SCFM is equivalent to a volumetric flow of .01 CFS at 6.25 ata. The crossectional area of the adsorber is .0668 sq. ft. and so the volume for five sections (which corresponds to the bed length assumed in Run 6C) is .1392 cu. ft. The residence time is therefore 13.92 V_o, or $\frac{E}{V_o} = 13.92$

Thus $(E)_{Pr} = \frac{9}{2}(1-V_o-V_2)\ 13.92 = 26.9$ using the same values of V_o and V_2 as previously. Before this can be compared with the empirically obtained value, the latter must be adjusted as well.

The value of A in the isotherm equation, $w = \frac{Ac}{1+Bc}$ contains a factor representing the crystal density (ρ_c = 1.56 gms/cc.). In fact, the density that should be used is an overall solid density, which allows for the presence of the binder. This, using Dworjanyn's[5H] figures again, works out to be 1.70 gms/cc. A should therefore have been larger by the factor of $\left(\frac{1.70}{1.56}\right)$, and accordingly E would have been smaller by the inverse factor. Thus the corrected value of E is $\frac{1.56}{1.70}\ 30.2 = 27.7$

$\underline{Y_F}$

Dworjanyn[5D, 5I] measured $\frac{D_c}{s^2}$ for 4A crystals using two different methods. His best estimate for this group was .14 sec^{-1}; the inverse may be used as an estimate for Y_F: 7.14 sec.

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Table of Symbols

A	crossectional area of empty adsorber vessel (sq ft)
A,B,A',B'	adsorption isotherm parameters
B'	initial slope of isotherm
C	gas concentration, relative to the feed concentration
C'	C at the outlet of the adsorber
D_c	crystal diffusion coefficient (cm^2/sec)
D_p	pellet diffusion coefficient (cm^2/sec)
E	Bed residence time $\left(\equiv \frac{LV_o}{V}\right)$ (seconds)
F	Fraction used in making next guess of C_i
F	gas flow rate (SCFM)
g	$\equiv \left(\frac{\partial w}{\partial r'}\right)_1$
g_p	$\equiv \left(\frac{3}{V_1 Y_F R^2}\right) X_F g$ value corresponding to g for use in the computer programme. Later, the subscript is dropped.
H	$\equiv \left(\frac{\partial C}{\partial l'}\right) \Delta l'$
k	$\equiv \left[\frac{9}{4} \frac{T}{E} B' \frac{P_s}{P'_s} \frac{P_R}{P'_R}\right]$ (used in choice of Q)
L	length of adsorber (ft)
l	length coordinate in adsorber (ft)
l'	dimensionless coordinate in adsorber length
P	pressure (ata)
$P_i(Y)$	polynomial in numerator of D_i
$P'_s(Y)$	polynomial in denominator of D_i
p	partial pressure (mm Hg)

Q	number of steps in bed length
q	weight percent of CO_2 adsorbed (%)
R	radial coordinate for pellets (cm)
R	number of steps in pellet radius
R'	dimensionless radial coordinate for pellets (=R/S)
r	radial coordinate for crystals (cm)
r'	dimensionless radial for crystals (=r/s)
S	radius of pellets (cm)
s	radius of crystals (cm)
s	number of steps in crystal radius
T	temperature (^oC or ^oK)
T	length of time-step (seconds)
t	time (seconds)
t'	dimensionless time (=t/T)
V	linear velocity of gas (in the empty adsorber vessel) (ft/sec)
V_o	void volume per unit volume of the adsorber
V_1	crystal volume per unit volume in a pellet
V_2	pore volume per unit volume of the adsorber
w	concentration in sorbed phase relative to feed concentration
$X_F = \frac{S^2}{D_p}$	"pellet resistance factor" (sec)
$X_R = \frac{S^2}{D_p E}$	

Y dimensionless group derived for use in the computer programme

$Y_F = \frac{s^2}{D_c}$ "crystal resistance factor" (sec)

$Y_R = \frac{s^2}{D_c E}$

Z dimensionless group derived for use in the computer programme

z length coordinate in cylindrical pellets (cm)

Matrices used in manipulation of crystal equations

$\underline{A}$ $\underline{B}$ $\underline{C}$ $\underline{D}$ $\underline{D}'$ $\underline{F}$ $\underline{I}$ (the unit matrix)

Greek letters

α shape factor for pellets

$\beta = \frac{2+2\alpha}{3}$

ρ_c crystal density (gm/cc)

Notes

1. $\dot{}$ above a symbol denotes the value for the preceding time step. For example, $\dot{g}_i$ is the previous value of g_i

2. The choice of some symbols was influenced by a desire to use the same symbol in the computer programme. For example Q,R,S,T,X,Y,Z. It is hoped that this has not resulted in unnecessary confusion in the use of symbols.

3. Since many of the symbols in the programmes are used with a variety of meanings, it is not practical to attempt to list them here.